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Mechanism and stereochemistry in the anionic polymerization of 1, 3-cyclohexadiene and the diimide hydrogenation of polymers/

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MECHANISM AND STEREOCHEMISTRY IN THE ANIONIC POLYMERIZATION OF 1,3-CYCLOHEXADIENE AND THE DIIMIDE HYDROGENATION OF POLYMERS

A Dissertation Presented

By

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February, 1972

To "P.J.," with affection, and with whom
I share the Ph.D.

ACKNOWLEDGMENTS

While writing, it occurred that my personal measure of value of the then new UMass PSE department was the ability to view my own participation with some considerable pride during the three and one-half years spent at Amherst as a research assistant. It is in this light that I acknowledge the professional staff of that department, and especially Dr. Robert W. Lenz, my thesis advisor, for a significant personal and educational experience.

The financial support for this work originated in the Office of Naval Research, Department of Defense (Themis fellowship), and the Office of Education, Department of Health, Education and Welfare (NDEA Title IV Graduate Fellowship), and was awarded by The University and the School of Engineering. This backing was of essential importance, and is now gratefully acknowledged.

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My parents, Louis A., and Anne F. Mango, are, after these many years, acknowledged and sincerely thanked for their support and the sacrifices which were made to enable me to complete the necessary undergraduate training and initially seek admittance to a doctorial program.

Finally, this work is most of all dedicated to P.J., an "affectionism" and first nickname used by me for my wife, Pam Jane. During our period at Amherst she provided the intense encouragement and support needed in those difficult, challenging moments which, in retrospect, I suspect form a common part of many graduate school experiences.

MECHANISM AND STEREOCHEMISTRY IN THE ANIONIC POLYMERIZATION OF 1,3-CYCLOHEXADIENE AND THE DIIMIDE HYDROGENATION OF POLYMERS

ABSTRACT

The mechanism of molecular weight limitation in the anionic polymerization of 1,3-cyclohexadiene has been studied using nmr and gas chromatographic techniques to detect and characterize benzene as a low molecular weight reaction byproduct of polymerization. This benzene is thought to occur by aromatization of cyclohexadienyl anions formed originally by abstraction of allylic protons from the monomer by the propagating polymeric carbanion. Such aromatization is part of a degradative chain transfer reaction sequence which limits molecular weight and conversion. Polycyclohexadiene endgroups were studied by ultraviolet spectroscopy which indicated that aromatization of the intermediate cyclohexadienyl anion occurred in complete preference to the alternative possibility of chain reinitiation by the cyclohexadienyl anion, a process leading to molecular weight, but not conversion, limitation. The latter alternative requires one cyclohexadienyl terminal group to be present for each polymer chain reinitiated; if present, such groups should be readily

detectable in the ultraviolet spectrum but were not observed.

Considerable interest has existed in correlating the structure of polymers derived from diene monomers with polymerization conditions and data is available for several alicyclic diene polymers. In the present study, the structure of anionically polymerized polycyclohexadienes was characterized by nmr and infrared spectroscopy and showed the effect, on polymer structure, when the diene center was present within a six member ring. In the infrared studies, the variation of the C-H out-of-plane stretching deformations for several cyclic <u>cis</u> olefins (675-800 cm^{-1}) were compared to a number of polycyclohexadienes prepared under various polymerization conditions. A high 1,2-unit content was noticed for polycyclohexadienes polymerized in both solvating and non-solvating media. The result is unusual for non-solvating media and the preference for 1,2 addition is thought to be caused by difficult steric contacts between monomer and polymer ring methylene groups during propagation.

The nmr spectra of polycyclohexanes prepared by the quantatative hydrogenation of polycyclohexadienes were determined and related to the <u>cis</u> vs. <u>trans</u> placement of adjoining rings in the polymer backbone. Polycyclohexanes

derived from polycyclohexadienes which were polymerized in polar media exhibited broader resonance envelopes for the ring methylene protons when compared to the nmr spectra of polycyclohexanes derived from polycyclohexadienes originally synthesized in non-solvating media. Nmr spectra of cis and trans 1,2- and 1,4-dimethylcyclohexanes, which were used as model compounds, indicated this behavior was characteristic of increasing cis ring placement when the polycyclohexadiene precursors were synthesized in less solvating media.

Quantitative hydrogenation of polycyclohexadiene to polycyclohexane was effected by treatment of the polymer with diimide from the thermal decomposition of p-toluenesulfonylhydrazide (p-TSH) at elevated temperatures (110° to 160°C) in aromatic solvents. The final portion of this work extended the diimide reaction to a variety of unsaturated polymers. At a p-TSH-to-olefin ratio of 2.0, homopolymers of butadiene, polycyclohexadiene, and polyisoprene were quantitatively hydrogenated as were two styrene-butadiene copolymers. Alkyl branching at or near the residual polymer double bond, as in methyl rubber and poly-2,5-dimethyl-2,4-hexadiene, gave less than 50% hydrogenation. Polychloroprene was not hydrogenated by diimide (conversions less than 10%); this is in agreement

with the behavior previously observed for low molecular weight olefins.

The unsaturated polymers which were successfully hydrogenated were soluble and, hence, showed no excessive crosslinking. Polycyclohexane and polyisoprene, the only samples evaluated for molecular weight changes, exhibited no chain degradation.

Some qualitative kinetic data was obtained using per cent conversion vs. time data. Under the conditions of toluene reflux and p-TSH-to-olefin ratios of 1.5, the relative rates of hydrogenation for cis, trans and vinyl butadiene units was:

$$k_{cis} \simeq k_{trans} < k_{vinyl}$$

Byproducts from the diimide generation resulted in the introduction of 0.2 to 1.0% of p-$CH_3ØSO_2$- groups into the polymer based upon 100% of the double bonds originally present.

TABLE OF CONTENTS

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LIST OF TABLES

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LITERATURE REVIEW

HISTORICAL

I. Introduction and General Goals

Polycyclohexadiene is formed most effectively from the anionic polymerization of 1,3-cyclohexadiene (1,3-CHD). However, the maximum obtainable molecular weights to date by this procedure are limited to about 10,000-15,000, apparently as a result of poorly characterized transfer or termination reactions. Examples of this sort in "living polymer" systems are not numerous and their understanding at a mechanistic level would be of interest and could lead to development of a higher molecular weight material.

Polymerization of 1,3-CHD is also of potential interest from the viewpoint of polymer sterochemistry. Extensive, and sometimes elegant work has been done to relate polydiene microstructure to reaction conditions, polymer physical properties and monomer structure. In this regard, the effect of having the diene center present in an unstrained ring system has not been examined and represents a gap in the current state of this information.

In a broad sense, this thesis describes, first, mechanistic studies done to ascertain the reasons for molecular weight and conversion limitation in the anionic

polymerization of 1,3-CHD. Next, analytical methods developed to study polymer microstructure are described which allowed this parameter to be related to reaction conditions. Related to this stereochemical study, polycyclohexadiene was converted to polycyclohexane, a novel polymeric material, by the use of a diimide hydrogenation technique previously established for low molecular weight materials. The technique exhibited several potentially interesting synthetic features in its use with a polymeric substrate. Thus, the final portion of this work treats the extension of the diimide hydrogenation technique for use with unsaturated polymeric substrates.

II. 1,3-Cyclohexadiene--The Chemistry of the Monomer

A. The cyclohexadiene system. 1,3-CHD is known to be readily susceptible to several, usually unwanted, chemical transformations under quite mild conditions which can effect the polymerizability of this material. These include oxidation, dimerization, disproportionation, and isomeric rearrangement. Thus, various aspects of 1,3-CHD's known organic chemistry suggested several requisites in handling and preparation of 1,3-CHD prior to and during reaction. Certain of the techniques and experiments ultimately adapted were based on this behavior. The

relevant information is reviewed in this section.

B. Availability of 1,3-CHD. 1,3-CHD is available commercially in experimental quantaties from the Columbia Chemical Company and several preparations for this material are extant in the literature (1-5).

C. Physical properties of 1,3-cyclohexadiene and related substances. 1,3-CHD, 1,4-cyclohexadiene (1,4-CHD), cyclohexene and benzene, are constantly referred to in this work and their physical constants have been collected in Table R 1a,b for reference.

D. Thermal dimerization and disproportionation. Conjugated dienes such as 1,3-butadiene undergo 1,4 addition with dienophiles to yield Diels-Alder adducts. These reactions occur between 0°C and 200°C either in the presence or absence of solvents (8). The cisoid configuration of the diene is required for Diels-Alder addition. Thus, cyclic dienes which possess a locked-in cisoid configuration exhibit particularly enhanced reactivity as compared to open chain analogs (i.e., butadiene). For example, 1,3-CHD gives the maleic anhydride adduct in quantitative yield in benzene at room temperature (9, p 1446).

1,3-CHD may react with itself in a Diels-Alder fashion (10,11). This process proceeds via a diradical intermediate which yields both polymeric and disproportionation

TABLE R 1a

PHYSICAL CONSTANTS OF 1,3-CHD AND RELATED SUBSTANCES

Compound	Reference	MW	MP (°C)	BP (°C)	Density	n_D^{20}
1,3-CHD	7	80.14	-89.0	80.5	0.840	1.47548
1,4-CHD	7	80.14	-49.2	85.6	0.847	1.4725
cyclo-hexene	6	82.14	-103.7	83.0	0.8102	1.4451
benzene	6	78.11	5.51	80.1	0.879	1.5011

TABLE R 1b

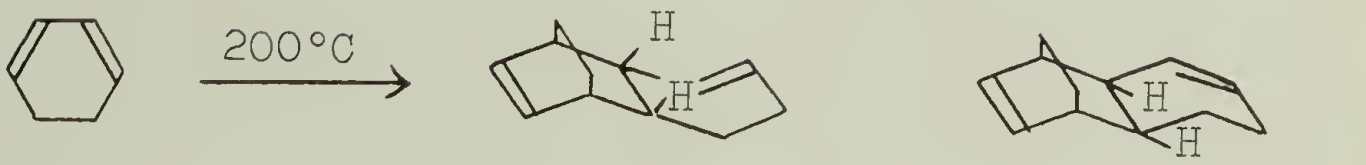
ULTRA VIOLET ADSORPTION PROPERTIES OF 1,3-CHD AND RELATED MATERIALS

Compound	Reference	Solvent	max.	max.
1,3-CHD	7	methanol	259 mu	10,000
1,4-CHD	7	n-hexane	224 mu	32
			270 mu	3
cyclohexene	7	methanol	207 mu	450
benzene	7	methanol	243 mu	158
			249 mu	200
			256 mu	252
			261 mu	158

products in addition to dimers. Initial studies at 200°C in bulk (11,12) established two major products of the thermal dimerization (Figure R 1a). Recent reports (13, 14,15) indicate that dimerization and disproportionation are competing processes with thermal (radical) polymerization. The relative extent of these reactions depends only on temperature, and both proceed by an open chain, diradical mechanism (Figure R 1b).

Kinetic results for $R = -d(1,3\text{-CHD})/dt = k(1,3\text{-CHD})^2$, where $k = k_{dimer} + k_{polymer}$, gave $k = 8.48 \times 10^2 \exp(-13.1 \text{ kcal/RT})$. At 200°C, $k_d/k_p = 1.21$, a ratio which increases as the reaction temperature is decreased. At 100°C, k was found to be 1.8×10^{-5} cc/mole-sec, while the calculated value at 0°C is 3×10^{-8} cc/mole-sec or about 1/600 the rate at 100°C. At 100°C, 30% of the original monomer was observed to be converted to dimer, polymer and disproportionation products in twenty-five hours. Thus, it might be anticipated that roughly 0.5 to 1% per month of an initially pure 1,3-CHD sample would be converted upon storage at 0°C! In one study (16) a synthesis of 1,3-CHD analyzed by gas chromatography gave 96.9% 1,3-CHD, 1.7% cyclohexene, and 1.4% benzene. Twelve hours storage at 0°C gave the analysis 94.4% 1,3-CHD, 2.6% cyclohexene, and 3.0% benzene. Presumably the disparity in the relative

FIGURE R 1a. Products in the Thermal Dimerization of 1,3-CHD.

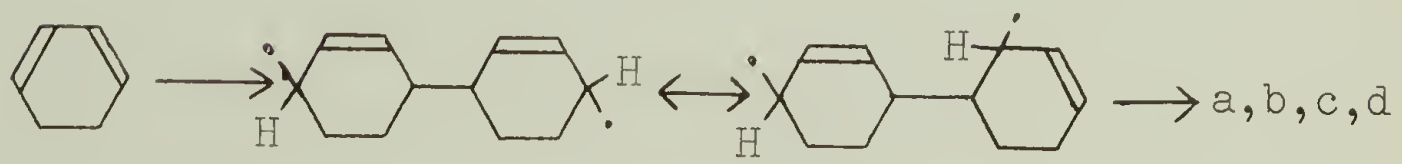


endo isomer
major product
b.p. 226C/746mm

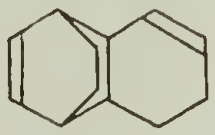
exo isomer
minor product
b.p. 229C/746mm

endo/exo = 4/1

FIGURE R 1b. Open-chain Diradical Mechanism of the Dimerization of 1,3-CHD.

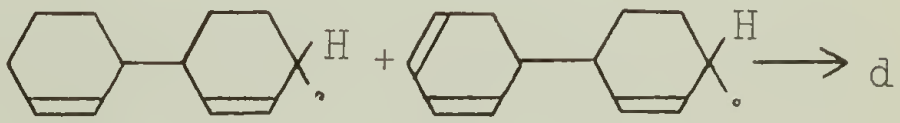


a. Intermolecular coupling

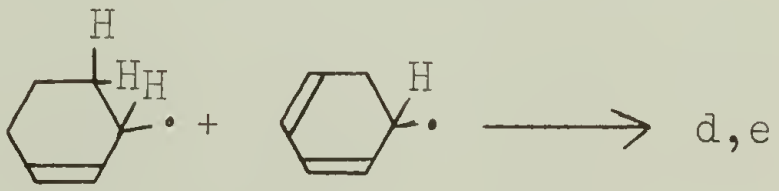


endo and exo dimers

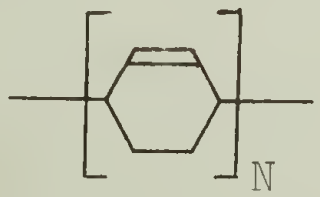
b. Disproportionation



c. Intermolecular Rearrangement



d. Intramolecular coupling



e. Dismutation

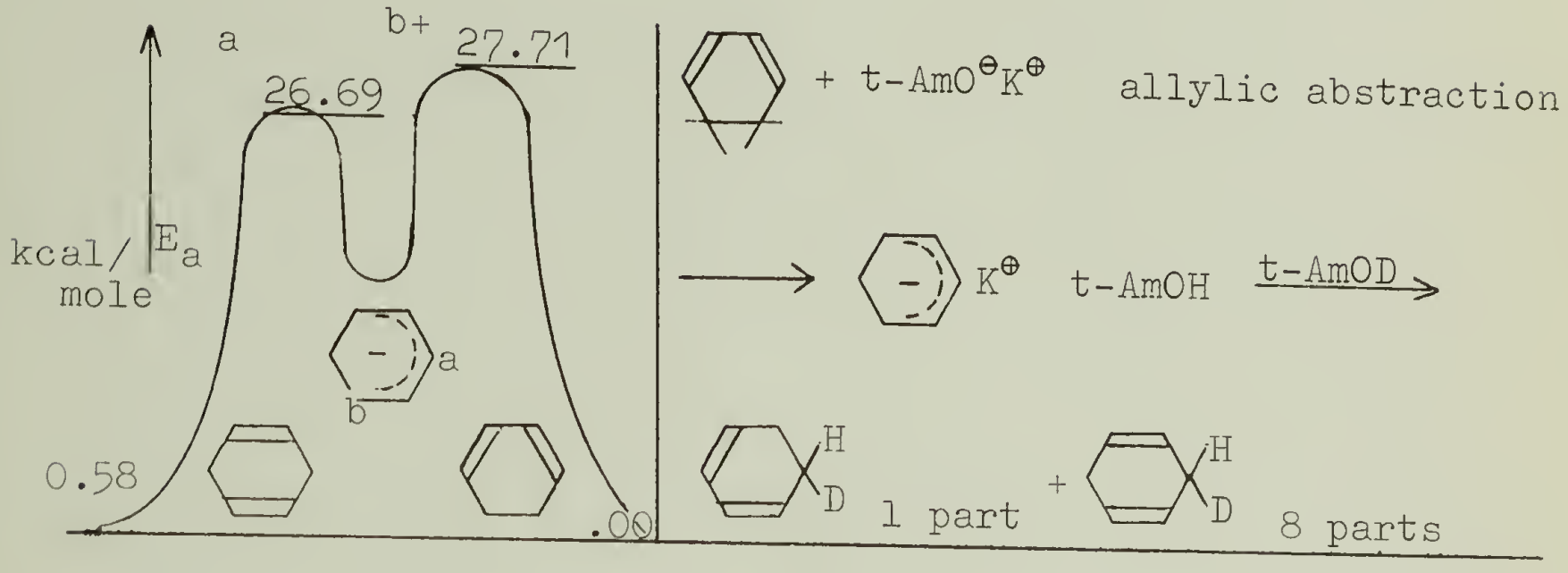
amounts of cyclohexene and benzene is accounted for by the inertness of the latter while cyclohexene may still undergo various reactions. The effect of oxygen is to slightly increase the conversion rate and modify the dimer/polymer ratio in favor of the dimer. Thus at 200°C and 20 hours with [1,3-CHD] = 9M in benzene, 1.1×10^{-4}M O_2 changes the conversion from 74% to 80%, and dimer to polymer ratio from 1.38 to 3.76.

E. Base induced isomerization and allylic abstraction of 1,3-CHD. The propagation sequence in anionic polymerization involves addition of monomer units to the terminus of a "polymeric" carbanion, a process which can also involve the counterion depending upon the solvating power of the medium. Since the polymeric carbanion is a strong (organic) base, the known behavior of the monomer in the presence of bases may act as a guide to processes which can occur during polymerization. Clearly, if processes other than addition occur, these will limit molecular weight, and possibly, conversion.

Bates, Carnigham and Staples (18) made such a study on the cyclohexadiene system. In separate reactions, pure 1,3-CHD or 1,4-CHD were isomerized with potassium tert-amyl oxide in tert-amyl alcohol-O-d^6 for 45 minutes at 95°C (Figure R 2). The isomerizations were held to low

conversion to prevent polydeuteration (<0.3%).

FIGURE R 2. Base Induced Isomerization of 1,3-CHD.



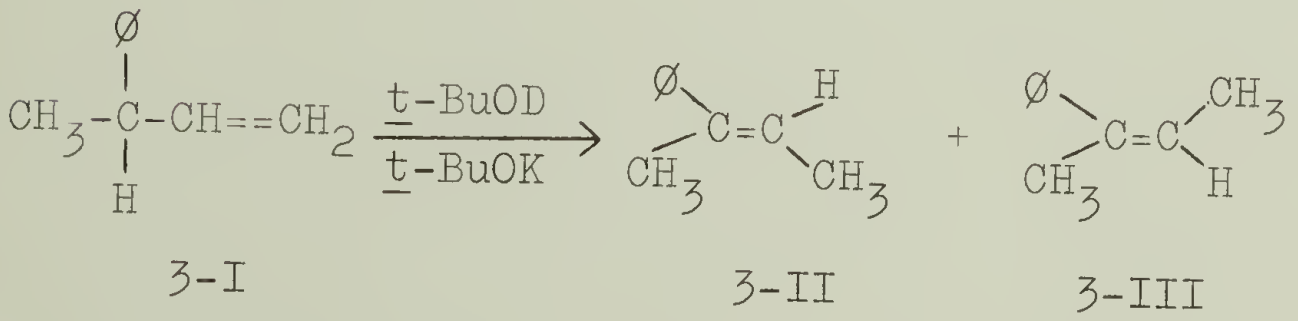
Analysis of the products by mass spectroscopy indicated that position "a" was protonated eight times as fast as position "b" (see Figure R 2). Since the result was the same using either pure 1,3-CHD or 1,4-CHD as starting material, a common allylic anion was apparently involved. Using additional rate data, the authors were able to construct the activation energy-reaction coordinate profile given in Figure R 2. It indicates that the collapse ratio for the cyclohexadienyl anion follows the Hughes-Ingold rule (19):

> . . . when a proton is supplied by acids to the mesomeric anion of weakly ionizing tautomers of markedly unequal stability, then the tautomer which is most quickly formed is the thermodynamically least stable; it is also the tautomer from which the proton is lost <u>most quickly</u> to bases.

For 1,3-CHD this results in reprotonation of the anion to preferentially form the thermodynamically less favored 1,4-CHD isomer in the observed 8 to 1 ratio. Of particular importance, allylic abstraction and isomeric rearrangement are seen to be viable alternatives to addition when 1,3-CHD is in the presence of carbanions.

The process discussed above was an intermolecular isomerication, and as such required a separate exchanging species (i.e., the solvent, tert-amyl alcohol-OD) to be present. However, such isomerizations are known to proceed intramolecularly. Thus 3-phenyl-1-butene (3-I) was observed to isomerize in tert-butyl alcohol-OD-potassium tert-butoxide to cis and trans 2-phenyl-2-butene (3-II,III) with 54% intramolecularity (26).

FIGURE R 3. Intramolecular Isomerization in the 3-phenyl-1-butene system.

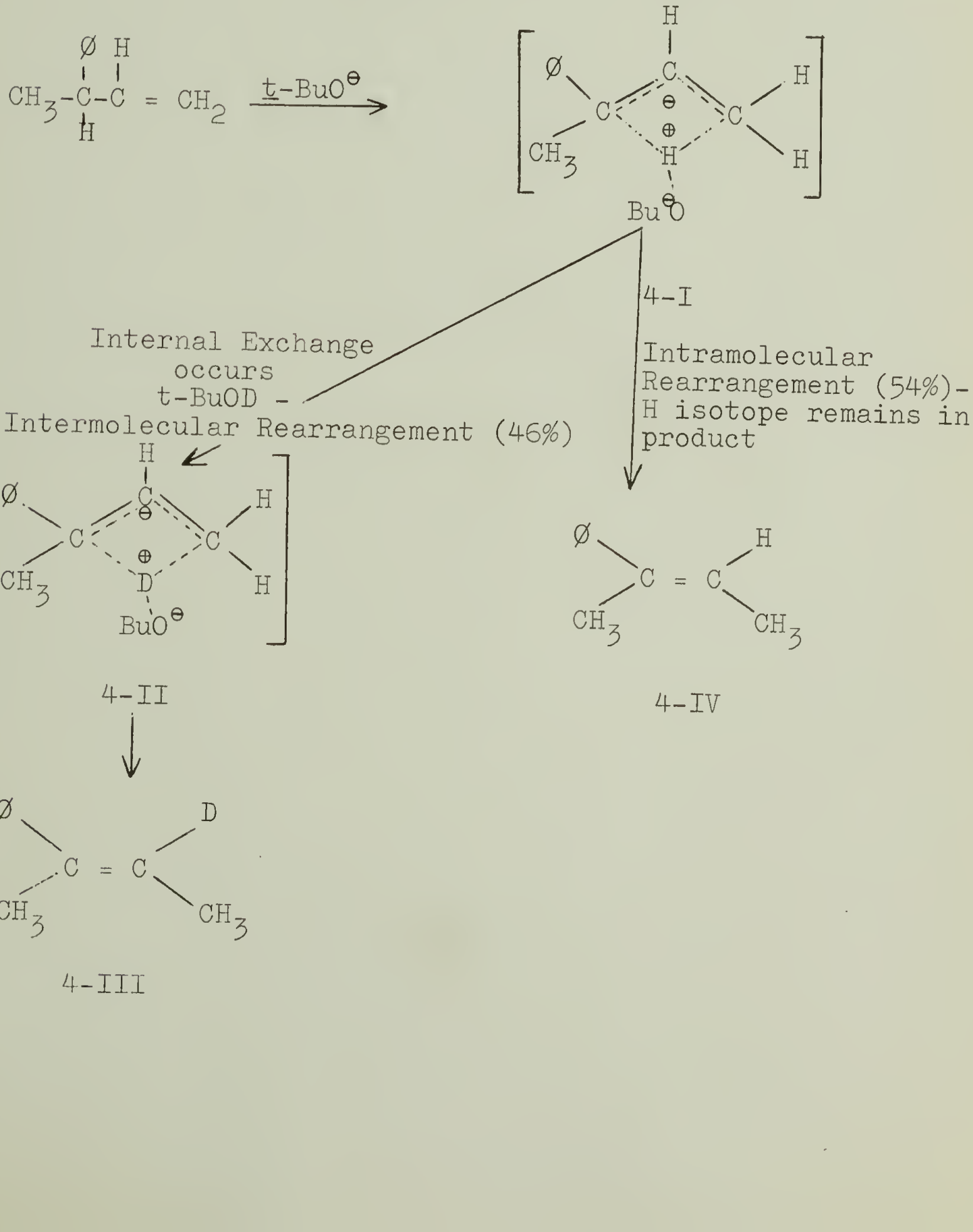


3-I 3-II 3-III

Intramolecular rearrangement was greatest in non-dissociating media (27). Thus, in going from ethylene glycol to tert-butyl alcohol, the ratio increased

((Intra)/(Inter)) from .14 to .30. A mechanism was postulated which involved the leaving group becoming concurrently hydrogen bonded at both anionic sites (Figure R 4).

FIGURE R 4. Mechanism for Intramolecular and Intermolecular Rearrangement of 3-phenyl-1-butene by potassium-t-butoxide.



To provide the best geometry, the hybridization was thought to be between sp^2 and sp^3 with the C-C-C bond angle decreasing to less than 120°. Collapse of the discrete intermediate (4-I) then gave the intramolecularly rearranged product (4-IV). Alternately, the hydrogen bonded leaving group may first exchange with molecules of the opposite isotropic type in the medium before the transition state collapses (4-II). This route yields the intermolecular product (4-III).

If such an isomeric rearrangement was active during the anionic polymerization of 1,3-CHD (see Historical, Part III, Polymerization Chemistry of 1,3-CHD), and produced small amounts of 1,4-CHD, the effect would be considerable as summarized in Table R 2 (20).

In summary, the 1,4 isomer does not homopolymerize anionically and its presence during the anionic polymerization of 1,3-CHD reduces molecular weight and conversion. Being activated by two double bonds, the allylic protons of 1,4-CHD are especially acidic. With four allylic protons, 1,4-CHD is apparently a particularly deleterious chain transfer agent in 1,3-CHD polymerization.

This possibility was investigated further in an unpublished nmr study by Lenz and Adrain (39). In an nmr tube, 1,4-CHD was contacted with n-butyllithium in hexane (1.6M)

TABLE R 2

COPOLYMERIZATION OF 1,3-CHD WITH 1,4-CHD

1,3-CHD	1,4-CHD	n-butyllithium	Polymerization		Per Cent Conversion	(η)
			Temperature (°C)	Time (hr)		
10	. .	0.6	30	40	100	0.22
. .	11	0.4	30	100	. .	. .
6	12	0.45	25	40	40	0.1

and the nmr spectra of the solution determined as a function of time. No change occurred for contact times up to five days. Addition of tetrahydrofuran (THF), however, caused a rapid loss of 1,4-CHD peaks (2.62ppm;5.67ppm) and growth of a singlet peak attributable to benzene (7.34ppm) (Table R 3).

TABLE R 3

THE AROMATIZATION OF 1,4-CHD WITH n-BUTYLLITHIUM IN TETRAHYDROFURAN AT 35°[a]

Time (min)	Peak Height Ratios[b] benzene-1,4-CHD
0 to 5 days, hexane only	no observed change
0 (from time of THF addition)	0.44
6	3.11
9	5.00
15	11.20
21	18.0[c]

[a]Operating temperature of Varian probe.

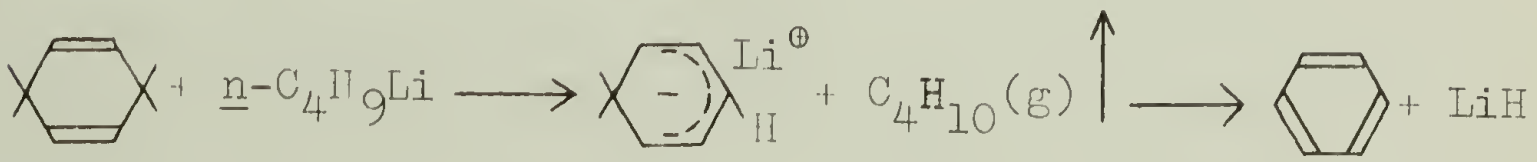
[b]Sample of 1,4-CHD contained a small amount of benzene as an impurity.

[c]Reaction completed.

Experimental Conditions: 1.3ml of 1.6M n-butyllithium was added to 0.2ml (170mg) 1,4-cyclohexadiene in a standard nmr tube purged before and after addition with nitrogen and capped. After 5 days, two drops (0.05 to 0.1 ml) of tetrahydrofuran was added.

Apparently, reaction between n-butyllithium and 1,4-CHD proceeds slowly or not at all in non-polar solvents at room

temperature. This is possibly a kinetic problem related to the tendency of n-butyllithium to form unreactive self-aggregates in aliphatic media. With the addition of a small amount of tetrahydrofuran the aggregates became solvated and reaction subsequently occurred. A white solid was formed during this reaction which reacted vigorously with water and exhibited a strong flame test for lithium after water treatment. Therefore, the following allylic abstraction and aromatization reaction was thought to take place under these conditions:



$$LiH + H_2O \longrightarrow H_2(g) + LiOH$$

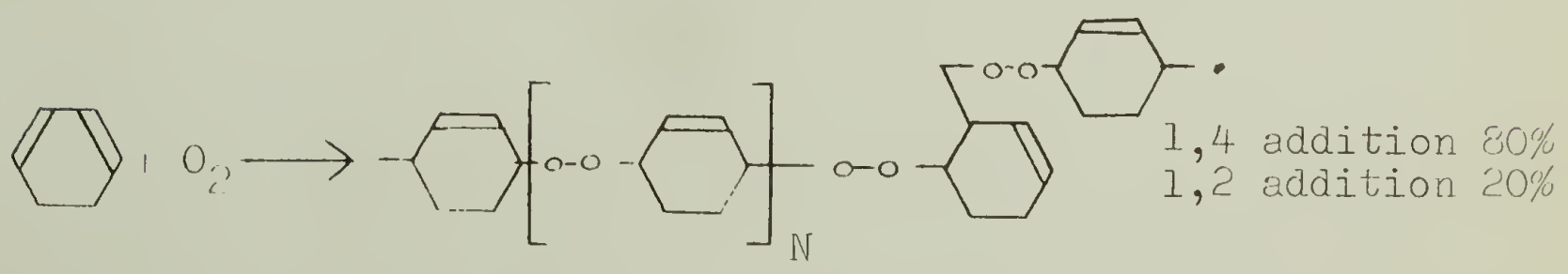
The results are consistent with the previous Japanese work and, further, suggest a specific termination sequence which would kill the kinetic chain if the abstracting species were a polymeric carbanion. Further, the apparent formation of the cyclohexadienyl carbanion as an intermediate, and the Bates et al. work which indicates this is a common species in the allylic abstraction (by bases) of 1,3- and 1,4-CHD, suggests 1,3-CHD may undergo a similar reaction (though to lesser extent) during its polymerization.

F. Effect of oxygen and oxidation on cyclohexadiene. Compounds containing allylic hydrogen atoms react with oxygen to form peroxides. This process is particularly rapid with 1,3-CHD and 1,4-CHD and the polar products formed would be injurious to anionic polymerization. There are two principal oxidation routes for 1,3-CHD: oxidation by excited singlet oxygen, and autoxidation. The former can be light induced and leads to the formation of 5,6-dioxabicyclo(2.2.2) octene-2, "norascaridiol" (Figure R 5)(22).

FIGURE R 5. Photo-oxidation of 1,3-CHD.

Of more practical interest, the products (23,24) and kinetics (25) of the auto-oxidation of 1,3-CHD in the liquid state have been evaluated and reviewed. Auto-oxidation of 1,3-CHD in bulk at 30°C and 960mm O_2 gave the interesting polymeric peroxide depicted in Figure R 6.

FIGURE R 6. Polymeric Peroxide Formed in the Auto-oxidation of 1,3-CHD.



The polymer is a clear, viscous liquid having a molecular weight average of 550 corresponding to a $\overline{DP}$ of 5 or 6. A microstructural analysis was performed via gas chromatographic and nmr techniques and indicated addition was 80% 1,4 and 20% 1,2. The rapidity of this process can be appreciated from the results of Howard and Ingold (25). The oxidations were performed at 30°C in chlorobenzene. Results for 1,3-CHD, 1,4-CHD, cyclohexene and a few additional hydrocarbons selected for comparison are given in Table R 4. In all cases the protons abstracted are

TABLE R 4

RATES OF AUTO-OXIDATION FOR CYCLOHEXADIENES AND RELATED MATERIALS

Material	$k_p/\ 2k_t \times 10^5$	$k_{abstr.}/H$	$k_t \times 10^{-6}$
1,4-CHD	230	1.5	2.8
1,3-CHD	10,000	55	33
cyclohexene	3,900	370	630
bibenzyl	13	0.14	10
indane	170	1.2	4.1
tetralin	230	1.6	3.8

Above k's are defined by:

$$RO_2. + RO_2. \xrightarrow{2k_t} \text{inactive products}$$

$$RO_2. + RH \xrightarrow{k_p} ROOH + R.$$

secondary, and since k_{abstr}/H is normalized to allow for statistical factors, the values given are direct measures of relative C-H reactivity. Two factors are apparent. First, $k_p/ 2k_t$ ratio, a measure of kinetic chain length, is relatively large for 1,3-CHD and 1,4-CHD. This is consistent with the observed formation of the polymeric peroxides. Secondly, as measured by k_{abstr}/H, the allylic hydrogens of 1,3-CHD and 1,4-CHD are 100 to 1000 times more liable than those of structurally similar hydrocarbons.

G. Conclusion. Several important aspects of the chemistry of cyclohexadiene are apparent in the preceding discussion. First, the monomer should be stored in the cold and handled under oxygen-free, inert atmosphere. Such precautions are required to minimize the formation of various impurities which include dimers, disproportionation and oxidation products. Firstly, polymeric peroxides form under mild conditions and would be particularly detrimental to anionic polymerization. Secondly, it is necessary to vacuum distill the monomer at low temperatures just prior to use to remove all impurities except benzene and cyclohexene which apparently would not effect the polymerization. Because of closeness in boiling points and structure, and the in situ formation of cyclohexene, benzene and dimer from 1,3-CHD upon heating, special separation means are

required to remove these latter substances when this is required for certain studies. Preparative scale gas chromatrography is particularly useful for this purpose. The potential of the polymeric carbanion to undergo allylic abstractions or isomeric rearrangements of the monomer appear to be possibilities which have yet to be evaluated. These factors may account for molecular weight and conversion limitations encountered by previous workers in attempted polymerizations of this monomer. Some of the studies reported on in the latter part of the thesis have been designed to test the validity of this assertion, and to suggest experimental corrections.

III. Polycyclohexadiene Polymerization Chemistry

A. Prior polymerization procedures. 1,3-CHD was first polymerized thermally by Hofmann and Damm in 1925 (10). Since then, all the conventional initiation methods have been used to effect polymerization of 1,3-CHD. These include anionic (3,4,20,21), cationic (16), radical (3 and references therein, 18-20), Ziegler-Natta (28), and irradiation (3). The use of thiourea canal complexes (29) and transannular polymerization of 1,4-CHD (30) to give polycyclohexene have also been described. As summarized in Table R 5, all attempts reported to date gave polymer

TABLE R 5

COMPARISON OF VARIOUS PROCEDURES USED TO POLYMERIZE 1,3-CHD

System	Solvents	Temperature (°C)	[η]	Reference
Catiomic				
$SnCl_4/Cl_3COOH$	toluene	0	0.04 to	27
	methylenechloride	0	0.12	27
BF_3/Et_2O	toluene	0	0.04 to	27
	methylenechloride	0	0.12	27
Ziegler Natta	toluene	50	0.05	28
$TiCl_4/Al(isoBu)_3$	benzene	5	0.03 to 0.12	28
Al-Ti ratio	cyclohexane	25	0.08 to 0.14	28
0·9 to 10	n-heptane	-75 to 50	--	28
Radical	--	80	$\overline{DP}$ 12	3
Ultraviolet	--	25 to 80	$\overline{DP}$ 12	3
Anionic				
n-butyllithium	toluene	25	0.11 to 0.23	4
initiator	benzene	25	0.11 to 0.23	4
	tetrahydrofuran	-80 to 50	0.03 to 0.12	4
Thiourea canal complexes	--	--	insoluable	3

molecular weights under 20,000 and conversions less than 80%. The best molecular weights and conversions were obtained with anionic polymerication in aromatic hydrocarbons at low temperature. This particular technique is of interest here and will be considered in detail.

B. Anionic polymerization of 1,3-CHD. The first reported anionic polymerization of 1,3-CHD was published by Lefebvre and Dawans in 1964 (3), with subsequent and related studies by Cassidy, Marvel and Ray (4) and Lussi and Barman (21). A wide range of solvents, temperatures, and monomer to initiator ratios have been utilized. Regretably, the relationship of reaction conditions to polymer properties and structure is obscured by apparently inconsistent data between, and even within, the three studies above. These inconsistencies are probably due to one or more of the following: (1) failure to identify distinct initiation and propagation sequences when working in non-polar media with n-butyllithium initiator, (2) reactions (chain transfer) competing with normal propagation, and (3) insufficient care in the handling and purification of reagents, possibly leading to formation of polar impurities which can inhibit polymerization. For these reasons, quantitative data on this polymerization is lacking and general trends are sometimes difficult to identify.

In the ensuing paragraphs data has been selected from the references for comparison where a correlation is thought to exist. However, it is emphasized that the information is sketchy and of a qualitative sort.

C. Molecular weight, conversion, and reaction conditions in the polymerization of 1,3-CHD. Sufficient data appears to exist to correlate molecular weight and per cent conversion with temperature, solvent, counterion, and monomer to initiator ratio. The data is collected into Tables R 6a to R 6d. When reported, the polymerization times were 3 days or longer, which hopefully was sufficient time to achieve near the maximum conversions and molecular weights possible with each set of experimental conditions examined.

The effects of temperature for reactions in polar (i.e., tetrahydrofuran, dimethoxyethane) and non-polar media (i.e., benzene, toluene) are presented in Table R 6a. The results of two independent sets of experiments indicate molecular weight and conversion increase as the reaction temperature is lowered in all four solvents. This is consistent with and suggests the possibility of chain transfer reactions occurring in addition to the normal propagation reaction. Normally these reactions have different temperature dependencies so the ratio

TABLE R 6

EFFECT OF REACTION PARAMETERS ON MOLECULAR WEIGHT AND CONVERSION IN THE POLYMERIZATION OF 1,3-CHD

TABLE R 6a--EFFECT OF TEMPERATURE

Temperature (°C)	(M)/(Li)	$[\eta]_{inh}$	Per Cent Conversion	Reference
		Tetrahydrofuran, Li counterion		
-80	16	0.115	85	4
-20	16	0.056	84	4
+25	16	0.054	71	4
+50	16	0.037	79	4
-30	60	0.175	..	21
-14	60	0.156	..	21
0	60	0.138	..	21
+14	60	0.132	..	21
+26	60	0.121	..	21
		Dimethoxyethane, Li counterion		
-32	60	0.160	..	21
-13	60	0.126	..	21
+20	60	0.095	..	21
+28	60	0.091	..	21
		Benzene, Li counterion		
-20 (?)	162	0.131	3.5	4
+25	162	0.212	54	4
+60	162	0.110	2.4	4
+24	..	0.234	..	21
+46	..	0.210	..	21
+63	..	0.181	..	21
		Toluene, Li counterion		
0	..	0.256	..	21
+20	..	0.236	..	21
+50	..	0.200	..	21
+60	..	0.190	..	21

TABLE R 6--Continued

TABLE R 6b--EFFECT OF SOLVENT

Temperature (°C)	(M)/(Li)	Solvent	$[\eta]_{inh}$	Per Cent Conversion	Reference
+25	16	benzene	0.143	47	4
+25	16	tetrahydrofuran	0.054	71	4
+28	60	dimethoxyethane	0.091	..	21
+26	60	tetrahydrofuran	0.121	..	21
+24	..	cyclohexane	0.182	..	21
+24	..	cyclohexane	0.218	..	21
+24	..	benzene	0.234	..	21
+20	..	toluene	0.236	..	21
+30	166	tetrahydrofuran, bulk dioxane	..	55	3
+30	166	diethylether	..	65	3
+30	166	heptane, cyclohexane	..	75	3
+30	166	benzene	..	98	3

TABLE R 6--Continued

TABLE R 6c--EFFECT OF COUNTERION

Temperature (°C)	Solvent	Counterion	$[\eta]_{inh}$	Reference
-32	DME	Li	0.160	21
-32	DME	Na	0.170	21
-32	DME	K	0.139	21
+20	DME	Li	0.095	21
+20	DME	Na	0.112	21
+20	DME	K	0.072	21
-30	THF	Li	0.175	21
-30	THF	Na	0.188	21
-30	THF	K	0.120	21

TABLE R 6--Continued

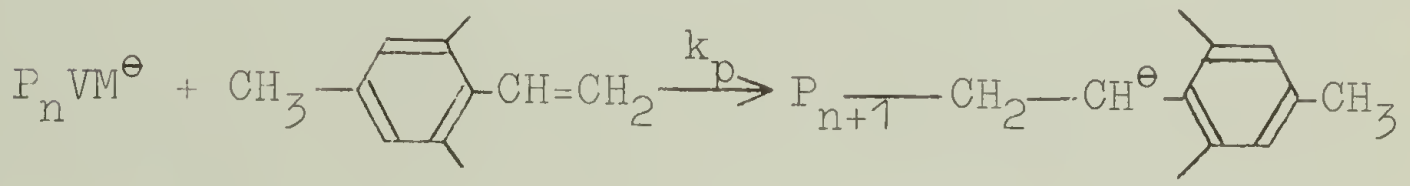
TABLE R 6d--EFFECT OF THE (MONOMER)/(INITIATOR) RATIO

Temperature (°C)	(M)/(Li)	$[\eta]_{inh}$	Per Cent Conversion	Reference
Tetrahydrofuran, Li counterion, small ratio				
+25	8	0.032	81	4
+25	12	0.036	80	4
+25	16	0.054	71	4
+25	32	0.079	40	4
Tetrahydrofuran, Na counterion, large ratio				
0	105	0.114	..	21
0	132	0.110	..	21
0	265	0.114	..	21
0	525	0.113	..	21
0	785	0.114	..	21

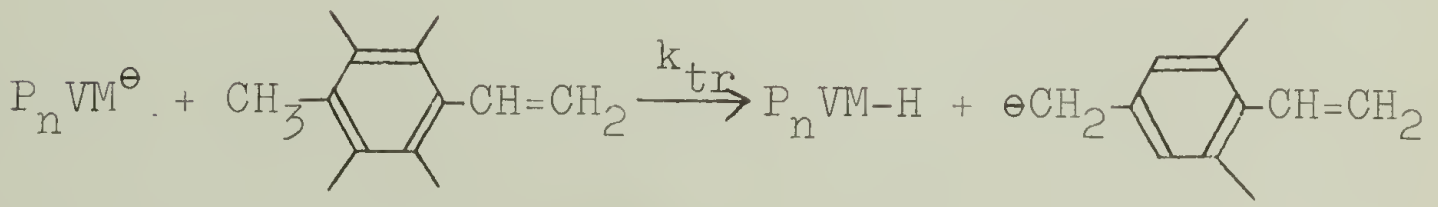
$k_{transfer}/k_{propagation}$ and the molecular weight varies with temperature at constant monomer to initiator ratios. The anionic polymerization of vinyl mesitylene in tetrahydrofuran ($Na^{\oplus}$ counterion) exhibits such behavior (32). Over the range -70 to +25°C the molecular weight of the polymer is temperature dependent. It was shown that the monomer may undergo normal propagation (Figure R 7a) or participate in a proton transfer reaction (Figure R 7b) which yields a carbanion too inactive to reinitiate polymerization. Lowering the temperature slows the rate of proton transfer more than the propagation rate, so molecular weight increases at lower temperatures.

FIGURE R 7. Variation of Molecular Weight with Temperature in Vinyl Mesitylene Polymerization

A.



B.



The effects of solvent are considered in Table R 6b. Generally, η_{inh} and per cent conversion increased in the order polar solvents < aliphatic solvents < aromatic solvents. The relation aliphatic < aromatic is reasonable on the basis that particularly slow initiation and propagation occurs in the former. In this case, termination by adventitious impurities is relatively more important. Also, we have since observed that the polymer is insoluble in aliphatic media, so that precipitation occurs and interferswith molecular weight and conversion. The fact that polar solvents such as tetrahydrofuran and dimethoxyethane give the lowest molecular weights and conversions may suggest two things. First, in contrast to aromatic or aliphatic solvents, these materials react with polymeric carbanions to form alkoxides and "dead" polymer chain ends. Secondly, tetrahydrofuran and dimethoxyethane solvate lithium counterions so that propagation is dominated by species wherein the counterion is "solvent separated" from the polymer carbanion (33, pp 410-413; Figure R 8). Perhaps these species more readily

FIGURE R 8. Nature of the Propagating Endgroup in Anionic Polymerization

$$P_n - M \rightleftharpoons P_n M \rightleftharpoons P_n \| S \| M \rightleftharpoons P_n - S + SM$$

P_n = polymer
M^n = metal
S = solvent

participate in reactions which lead to chain transfer or termination. This possibility remains to be evaluated.

The effects of varying the counterion are collected in Table R 6c. In tetrahydrofuran and dimethoxyethane the inherent viscosities are reduced with potassium and sodium as the counterion. This effect is possibly due to cluttering in the transition state by the relatively large sizes of sodium and potassium ions as compared with lithium. As will be discussed in detail later, the properties for this monomer embody difficult steric contacts among ring methylene groups. Large counterion size would be expected to aggrevate this situation, especially since these ions solvate poorly and thus remain in close proximity to the reaction center. These steric factors, then, would reduce molecular weight and conversion.

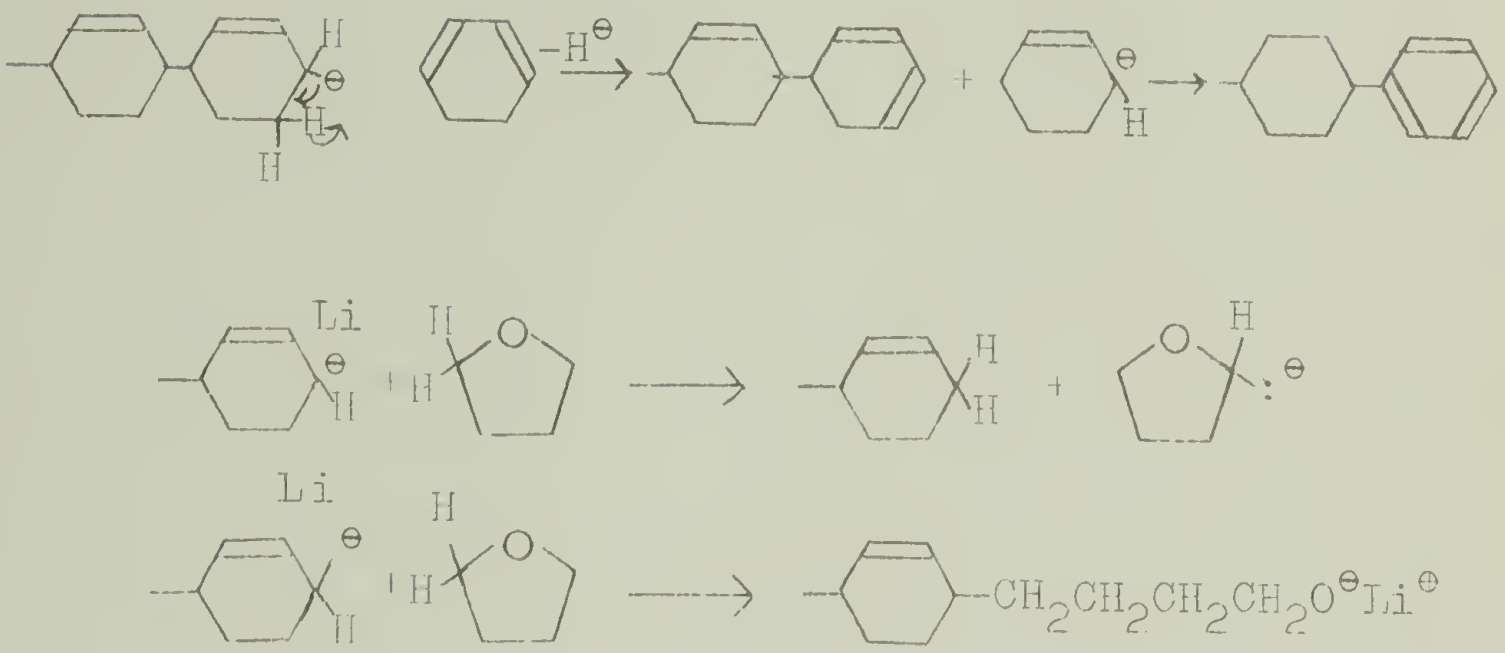
Table R 6d describes the effect of varying the monomer to initiator ration. In tetrahydrofuran with lithium counterion and monomer to initiator ratios from 8 to 32, molecular weight was inversely proportional to initiator concentration. This behavior is normally anticipated for rapid initiation and propagation which occurs in this solvent with lithium. In tetrahydrofuran with lithium counterion the monomer to initiator ratio was varied from 10% to 78% with essentially no change in the molecular

weight of the product. Here, it might be that at such high ratios the polymerization process occurred for all chains before the monomer completely reacted. In this regard, percent conversion data would have been useful.

D. Molecular weight limiting reactions in 1,3-CHD polymerization. The fact that less than theoretical conversions (<80%) and low molecular weight ceilings occur in 1,3-CHD anionic polymerization indicates that chain transfer or termination processes are active. This situation has been recognized by previous workers and two chain transfer schemes have been postulated.

A "hydride elimination" scheme was suggested by Lefebvre and Dawans (8) who noted that iodine titrations of several polycyclohexadienes indicated only 80% of the expected unsaturation (Figure R 9). Noting that the end-groups of such polymers should be apparent in the ultraviolet spectra of the polymers, Cassidy, Marvel and Ray (9) recorded the chloroform spectra of a sample synthesized in benzene. Bands were observed at 261.1, 254.7, 248.7 and 242 mu and thought to be consistent with the phenyl end-groups which result in the Lefebvre and Dawans scheme.

FIGURE R 9. Previously Suggested Termination Mechanisms in the Polymerization of 1,3-CHD (8).



Also, these authors postulated a possible reaction of the polymeric carbanion with the solvent in polar media as shown in Figure R 9. Abstraction reactions of this sort are well established except that attack is now thought to result in opening of the tetrahydrofuran ring to yield a lithium alkoxide (35).

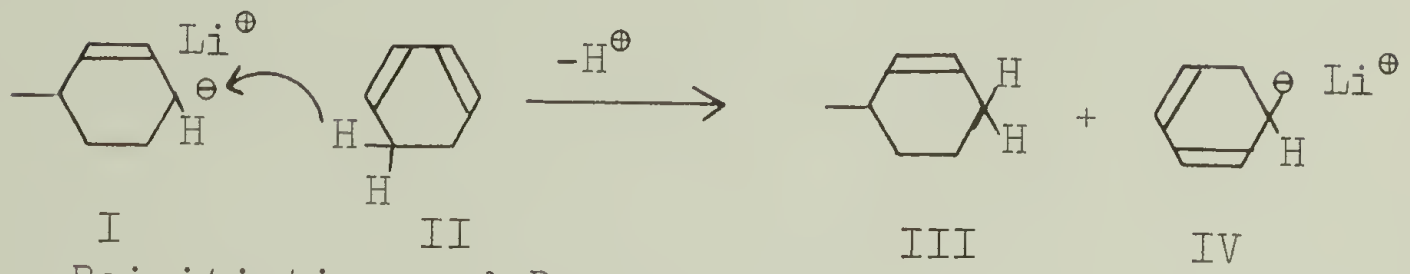
There are several possible shortcomings in the hydride elimination scheme. First, the cyclohexadienyl carbanion (9-II) was depicted immediately reinitiating polymerization which allows for limitation in molecular weight but not conversion. In fact, both are less than theoretical. Secondly, the iodine titration was not performed on a known standard (e.g., polybutadiene) nor was

the spectra of the polymer redetermined after titration. Thus, it is not known whether the 80% level of unsaturation represents lack of olefinic content or incomplete titration reaction. Also, at a level of 80% unsaturation the mechanism above would require molecular weight ceilings around 1500, and aromatic proton resonances clearly present in the polymer nmr spectra. In practice these circumstances are not observed. Further, the postulated rearrangement to phenyl endgroups generally requires elevated temperatures. The interpretation given the ultraviolet spectra are questionable because of the possibility of incomplete benzene removal (the ultraviolet adsorption maxima of benzene are 243, 249, 256, and 261 mu) and the use of N-phenyl-2-napthylamine as an antioxidant. Since both adsorb strongly in the ultraviolet, and large sample sizes were used (20 gm/l using 1 cm cells; molecular weights about 5000), these results appear subject to question.

As an alternative to the "hydride elimination" mechanism, Lussi and Barman (26) postulated the "allylic abstraction" scheme given in Figure R 10.

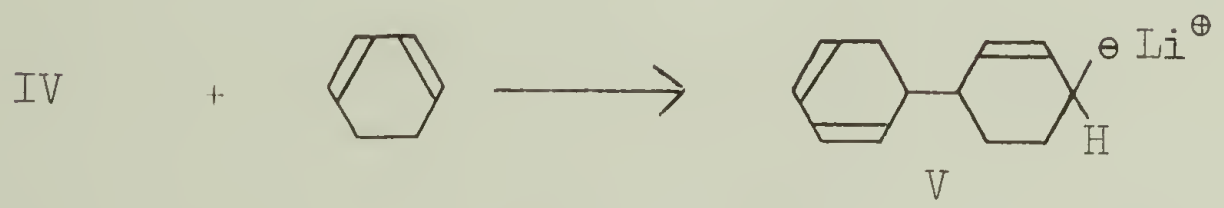
FIGURE R 10. Allylic Abstraction Scheme in the Polymerization of 1,3-CHD Previously Suggested.

a. Allylic Abstraction



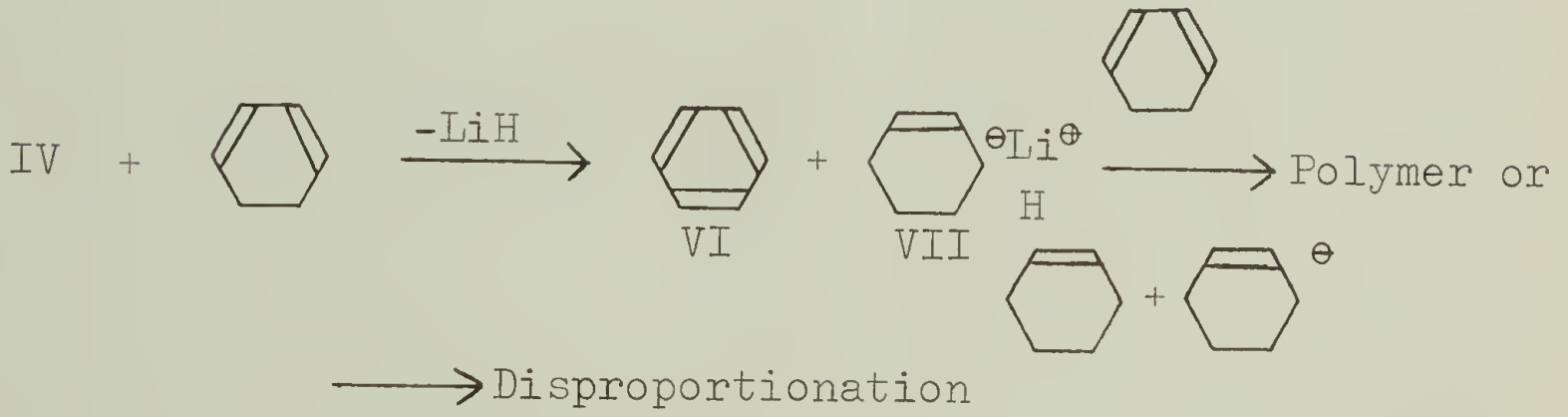
I II III IV

b. Reinitiation and Propagation



V

c. Hydride Elimination with Addition to a Second Monomer Unit



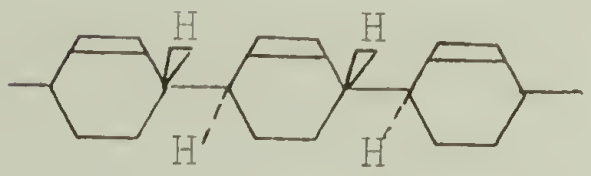
VI VII

The initial step is abstraction of an allylic proton from a monomer unit (II) by the polymeric carbanion (I) to terminate the polymer chain (III). The cyclohexadienyl carbanion so formed (IV) then either reinitiates another polymer chain (Figure R 10,b) or, in an unspecified manner, loses lithium hydride and forms the active species (VII) and benzene (VI). The active species (VII) may then

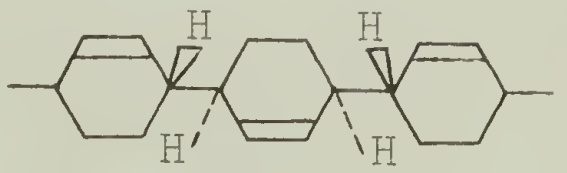
reinitiate, or disproportionate to form cyclohexene. Again, the overall process limits molecular weight, but not conversion.

E. Microstructure of polycyclohexene. The possibilities for tacticity, structural and geometrical isomerism in polycyclohexadiene are described in Figure R 11 a-d. The infrared spectrum of

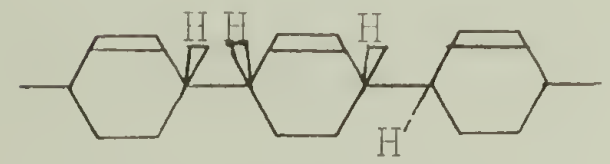
FIGURE R 11. Microstructure of Polycyclohexadiene.



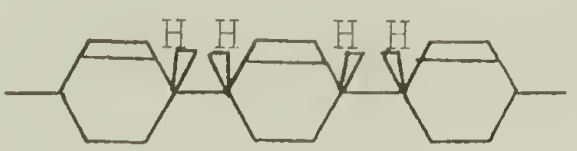
threo-diisotactic



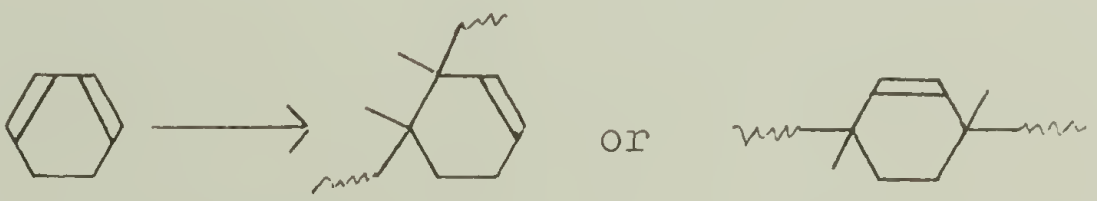
disyndiotactic



iso-syndiotactic

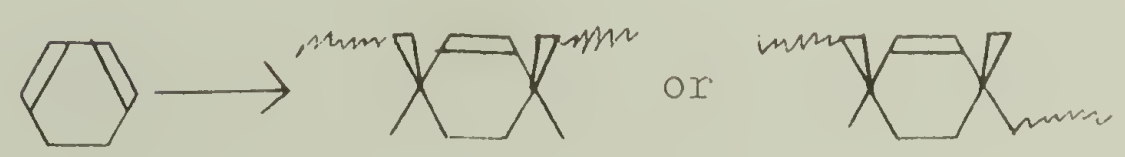


erythreo-diisotactic



1,2 addition

1,4 addition



cis-ring insertion

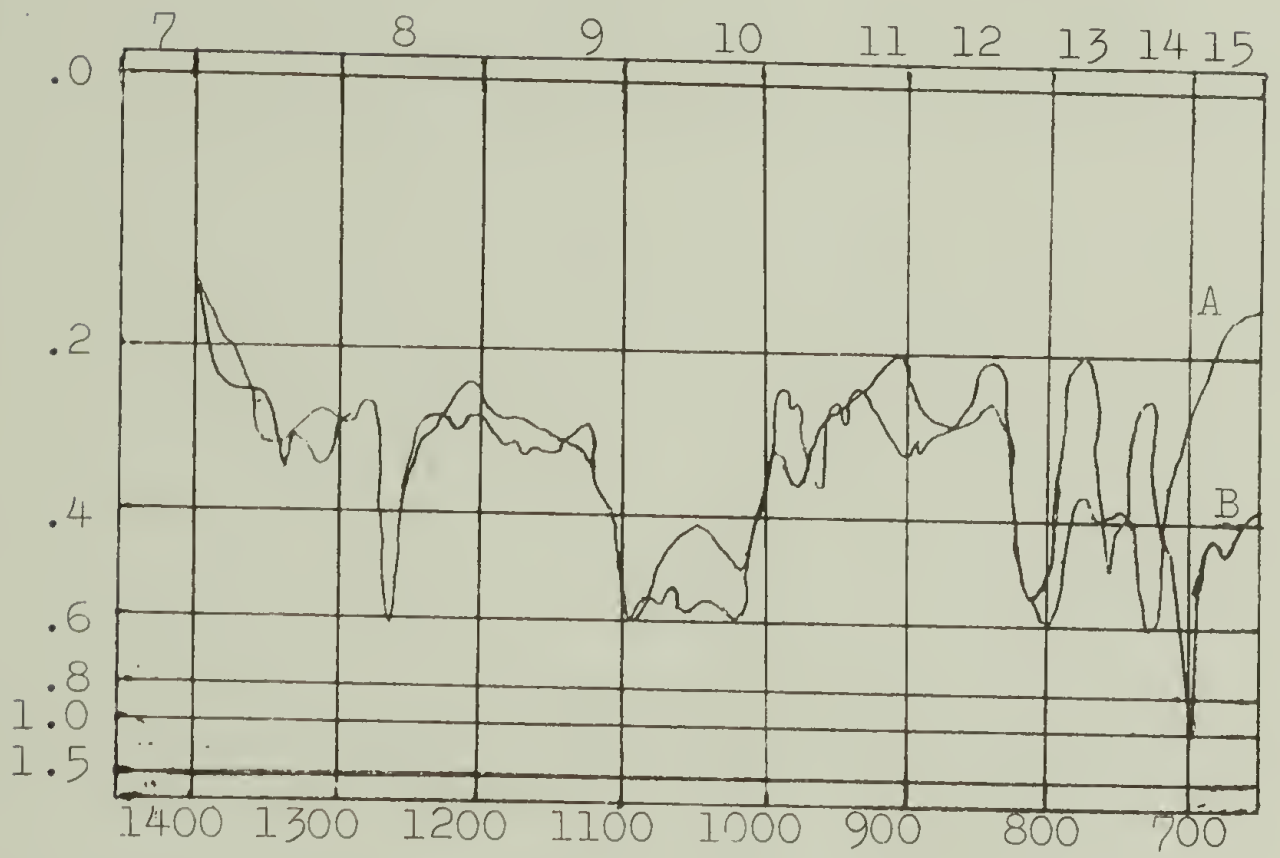
trans ring insertion

polycyclohexadienes synthesized arionically in dimethoxy-ethane and benzene, and by Ziegler-Natta catalysis (lithium aluminum hydride-titanium [IV] tetrachloride in various media) are consistent with a chain composed of cyclohexene repeating units (Figure R 12). General adsorbance occurs at 3015 cm^{-1} (olefinic C-H stretching), 1650 to 1680 cm^{-1} (C=C stretching), and between 700 and 800 cm^{-1} (disubstituted cis olefin C-H out-of-plane stretching deformation). Curiously, some confusion has existed on this latter assignment which is illustrated by a quote from the Lefebvre and Dawans article (3, p 3291):

> From the standpoint of their microstructure all polycyclohexadienes synthesized in non-complexing media are comparable, no matter what the iniator used. They are mainly composed of cyclohexene 1,4 substitution units, and the double bond configuration is cis and trans.

The authors assigned the adsorbance at 725 cm^{-1} to cis double bonds and a (small) peak at 975 cm^{-1} to trans double bonds. However, the residual double bonds in the polymer are part of cyclohexene structure units, and can occur only in the cis configuration. As noted in Figure R 11, cis/trans isomerism can occur, but this terminology refers strictly to ring placement. Further, it has since been noted by us that the 965 cm^{-1} band remains after the polymer has been completely hydrogenated, thus it is apparently not sensitive to geometrical

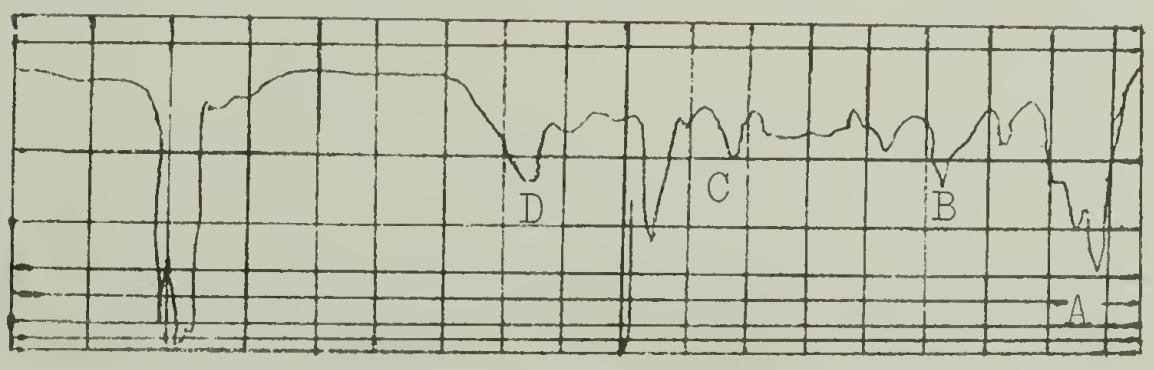
FIGURE R 12. Infra-red Spectra of Poly-cyclohexadienes Synthesized in Various Media.



Long wavelength region
of the Infrared

Curve A: Benzene

Curve B; Dimethoxyethane



Complete Infrared spectrum of Hydrocarbon Synthesized Polymer

peak A - 725 cm^{-1}
B - 975 cm^{-1}
C - 1310 cm^{-1}
D - 1680 cm^{-1}

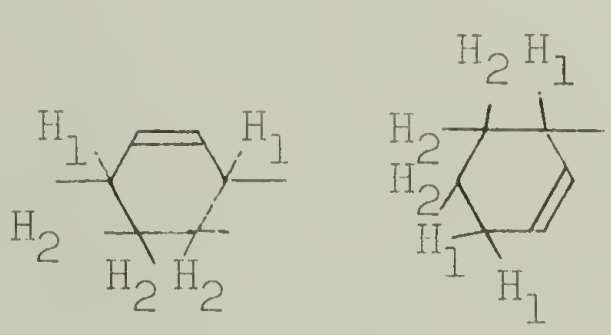
note the relative intensity of peaks B and C.

isomerism.

The infrared spectra does, however, contain useful information about repeating unit structure. Inspection of the spectra indicates that the adsorbance between 700 and 800 cm^{-1} changes in a characteristic fashion depending upon the conditions of synthesis. This particular observation has yet to be fully interpreted, or exploited in the literature as possibly indicative of microstructural compostion.

The nmr spectra of polycyclohexadienes have been determined and three broad peaks occur at 1.6, 2.0 (aliphatic) and 5.62 ppm (olefinic) respectively. In interpreting the spectra the non-olefinic protons in polycyclohexadiene were divided into those directly adjacent to the double bond (H_1; 2ppm) and those further removed (H_2; 1.6ppm) (Figure R 13). Thus, for complete

FIGURE R 13. Determination of 1,2 vs. 1,4 Addition in Polycyclohexadiene via NMR.



Dioxane, THF, Et_2O, DME $(H_1/H_2)_{obs.} = 1$

benzene, heptane $(H_1/H_2)_{obs.} = 2/3$

H_1 absorbs at 2 ppm

H_2 absorbs at 1.6 ppm

1,4 addition (H_1/H_2) = 2/4 = 1/2, while for only 1,2 addition (H_1/H_2) = 3/3 = 1. For polycyclohexadienes synthesized in tetrahydrofuran, dimethoxyethane, dioxane, and diethyl ether, the observed proton ratio value approaches 1, while in heptane, cyclohexane, and benzene the values are about 2/3, corresponding to approximately 70% 1,4 addition. The peaks in 60 MHz spectra were broad and considerably overlapped in the aliphatic region; only the aliphatic and olefinic proton resonances being completely resolved. Therefore, measurement of peak areas involves several per cent (10%?) error. There may also be a question of assignment. In various cyclohexenes substituted only on the ring olefinic carbons (e.g., 1- or 2-methylcyclohexene, 1,2-dimethylcyclohexene), it is true that the ring methylene protons resonate in two groups: those attached to carbon atoms next to, and those on carbon atoms further removed from the olefin bond. However, in the case of polycyclohexadiene, two of the ring methylene protons become methine protons and a corresponding shift upfield might be expected. For 1,4 placed units, the protons next to the double bonds are both methine protons, while the four further removed are all methylene protons. In this case it is likely that these two types of protons will exhibit distinct chemical shifts, and be observed at

two separate nmr resonances. However, in 1,2 ring placement, the set of protons next to the double bond is a mixture of one methine, and two methylene protons as is the set of protons further removed. In this case it seems questionable that each group should exhibit separate resonances.

F. Polar additives in the polymerization of 1,3-CHD. Reaction rates, and stereochemistry of addition are significantly altered when intentionally added polar materials are present during anionic polymerization reactions in non-polar media (41-45). Such materials have included inorganic lithium salts (41), lithium alkoxides (41, 42, 43), and pure polar liquids as tetrahydrofuran (44, 45). Some unpublished preliminary research on the effects of similar additives on 1,3-CHD-n-butyllithium polymerization has been conducted by Lenz and Adrian (38, 39). Present research on the 1,3-CHD system originally stemmed from that background material, which is summarized in this section.

One particularly interesting observation in the work of Lenz and Adrian was that when some additional n-butyllithium was added to reinitiate a 1,3-CHD polymerization in tetrahydrofuran at -78°C that had been inadvertently terminated by some adventitious carbon

dioxide gas from a cold bath, the product yield and molecular weight were apparently enhanced when compared with carbon dioxide free systems (Table R 7a,b). It was thought that a new catalyst system may have been formed in this reaction. However, information on the proposed new catalyst system was sketchy. It appeared that the system functioned well only in tetrahydrofuran at low temperature (-78°C), and that the modified catalyst might be heterogeneous rather than homogeneous. The latter thought was suggested first by the formation of a fine white precipitate upon addition of carbon dioxide to n-butyllithium (see later discussion), and by the altered nature of the products. Isolation of catalyst solid indicated large amounts of lithium were present (33% ash, 48% C, 8% H; strong lithium flame test) and gaseous evolution upon treatment with dilute acid was thought to suggest the presence of carbonate groups. In an alternate approach, compounds which could result from the reaction of butyllithium and carbon dioxide were added as co-catalysts in otherwise normal n-butyllithium-only polymerizations. These compounds included: 2-ethyl-n-caproic acid, butyric anhydride, propionic acid, valeric acid, lithium carbonate, dibutyl ketone and tert-butyl alcohol. However, none of these compounds

TABLE R 7a,b

COMPARISON OF POLYCYCLOHEXADIENES SYNTHESIZED IN THE PRESENCE AND ABSENCE OF POLAR ADDITIVES

Solvent	Catalyst	Temperature (°C)	Viscosity*	Softening Point (°C)	Yield (%)
a. Without Polar Additives					
toluene		room	0.15	. .	. .
tetrahydrofuran		0	0.05	70	low
tetrahydrofuran		-78	0.08	120-130	. .
bulk		room	0.17	124	12
b. With Polar Additives					
	$BuLi/CO_2(s)$		0.29	170-180	85
	$BuLi/CO_2(g)$		0.18	155-170	18
	$BuLi/CO_2(s)$		0.26	190	85

*$(\eta)int = KM^a = 3.2 \times 10^{-4} M_n^{0.73}$

produced the simultaneous combination of high yield and higher molecular weight observed with the in-situ preparation of the catalyst.

Carbonation of alkyl or aryl lithium reagents to produce either the corresponding acids (48, p 556) or ketones (49, p 128) has been known for some time and is summarized in Figure R 14. This chemistry may provide a guide to

FIGURE R 14. Carbonation of Lithium Reagents to Produce Acids or Ketones.

$$RLi + xs\ CO_2\ (s) \longrightarrow RCO_2Li \xrightarrow{H} RCO_2H$$

1. RLi added to CO_2 (s)
2. RLi sprayed into CO_2 (g) atmosphere

$$2RLi + CO_2\ (g) \xrightarrow{H_2O} R_2CO + 2LiOH$$

understanding the structure and function of the proposed new catalyst system. It is useful to consider the synthesis of the catalyst. The material was prepared either by adding (non-purified) carbon dioxide gas or a small piece of (non-purified) carbon dioxide solid to an organo-lithium solution causing immediate precipitation of a white solid and giving the solution a gelatinous character. The system was then purged with nitrogen or argon and incremental amounts of n-butyllithium were added until the color characteristic of the polymeric carbanion reappeared. Both

conditions approximate a situation where carbon dioxide is bubbled through or over an organo-lithium solution. Under such conditions Gilman and VanEss (36) have shown that phenyllithium forms benzophenone via a dilithium salt mechanism (Figure R 15). This proposed dilithium

FIGURE R 15. Formation of Benzophenone via Carbonation of Phenyl Lithium.

$$PhLi + CO_2 \xrightarrow[\text{reflux}]{Et_2O} PhCO_2Li\ (s)$$

$$PhCO_2Li + PhLi \xrightarrow{\text{fast}} Ph_2C\langle^{OLi}_{OLi}$$

$$Ph_2C(OLi)_2 + H_2O \longrightarrow Ph_2C = O + 2LiOH$$

intermediate was later isolated and characterized by Zook et al. (37). The di-salt hydrolyzed readily in air but was stable under nitrogen. In general, the reaction was best carried out in ethers, under nitrogen, either by normal or inverse addition of the reactents (40). Usually addition of gas to the organo-lithium yielded a white gelatinous precipitate (RCO_2Li) which may still prevail after addition of the second equivalent of lithium to this salt.

Based on this information, one might conjecture that the n-butyllithium-carbon dioxide catalyst combination of Lenz and Adrian consisted initially of a dilithium salt, $Bu_2C(OLi)_2$. Since the carbon dioxide used was not highly

purified, it is probable that residual moisture was present in the gas or condensed on the carbon dioxide surface. This water could convert some (perhaps all?) of the dilithium salt to dibutyl ketone and lithium hydroxide. Thus the new catalyst may have been a complex mixture of $Bu_2C(OLi)_2$, dibutylketone and lithium hydroxide of varying ratios depending on the amounts of water present and dilithium salt initially formed. These materials are quite polar and may be expected to interact strongly with the polymerizing center.

IV. Hydrogenation of Polymers

The hydrogenation of polymers has recently been reviewed in detail (49,50), and many specific examples of industrial interest are available in the patent literature. Thus only a few general remarks on this subject are made here to hopefully bring this current work into context.

Polymeric materials, especially polydienes, may be hydrogenated to derived structures which exhibit substantially altered physical properties and generally improved resistance to oxidative and thermal degradation. In practice, about 70 to 95% conversion is usually sought. The residual unsaturation allows potential sites for further treatments, such as vulcanization, which may be desired

during the final processing steps. Hydrogenation of polymers with branching within the repeating units generally yields rubbers, while linear polymers give partially crystallizable thermoplastic products. Thus, as per cent hydrogenation increases, 1,4-polybutadiene becomes an increasingly more crystalline thermoplastic with substantially altered tensile strength, elongation, stiffness and hardness properties (51). Alternately, poly-isoprene upon complete hydrogenation gives a 1:1 alternating copolymer of ethylene and propylene (52).

Polymers have been hydrogenated generally by one of three techniques, each having numerous permutations: (1) hydrogen gas with base metal and supported metal catalysts, (2) hydrogen gas with noble metal catalysts, and (3) organo-transition metal and organic metal salt combinations such as cobalt acetylacetonate with tri-isobutyl aluminum. The first two involve heterogeneous reactions, while the latter was shown to be homogeneous. Each method has numerous positive features and may represent the most advantageous procedure for specific applications; however, their collective shortcomings are of present interest. The procedures involve two or more catalyst components which must be compounded at some point before use. Usually, one or more of these materials are

air and moisture sensitive, and often times pyrophoric. During reaction the polymeric products physically entrain difficult-to-remove metallic residues which later adversely affect the quality of the product. Some of these systems, though not all, require elevated temperatures and pressure for reaction. Also, the heterogeneous procedures have the shortcoming of yielding nonuniformly hydrogenated products at less than 100% conversion--i.e., at partial conversion some polymer molecules remain essentially unreacted while others are nearly quantitatively converted (53). The product composition then resembles a blend instead of a homogeneous, partially hydrogenated homopolymer. Related to this, catalytic processes may also cause cis-trans isomerism of double bonds, and bond migration (54). Finally, heterogeneous catalysts in general are markedly susceptible to poisoning by impurities which may occur from various sources--particularly compounds containing sulfur.

Whatever the particular mechanistic features of these difficulties are, it appears that one essential factor is the presence of highly reactive organometallic intermediates in the system. Thus, a reagent which can successfully hydrogenate.polymer substrates, but which does not require an organometallic component, may form the basis for a

significant and useful addition to the techniques now used for polymer hydrogenation.

V. Hydrogenation with Diimide

The transitory species, diimide, has been extensively studied and its use as a general hydrogenation agent for low molecular weight olefins has been demonstrated. This chemistry has been the subject of recent reviews (55,56); the essentials of which form the basis for the following discussion.

Diimide, N_2H_2, is an azo compound which may be isolated below 120°K but readily decomposes into ammonia, nitrogen and hydrazine above this temperature (57,58). When used for synthetic purposes it can be generated *in situ* from several convenient precusor compounds (see later discussion). Structurally, the molecule exists either in a planar or zig-zag form (57) as shown in Figure R 16.

FIGURE R 16. Molecular Structure of Diimide.

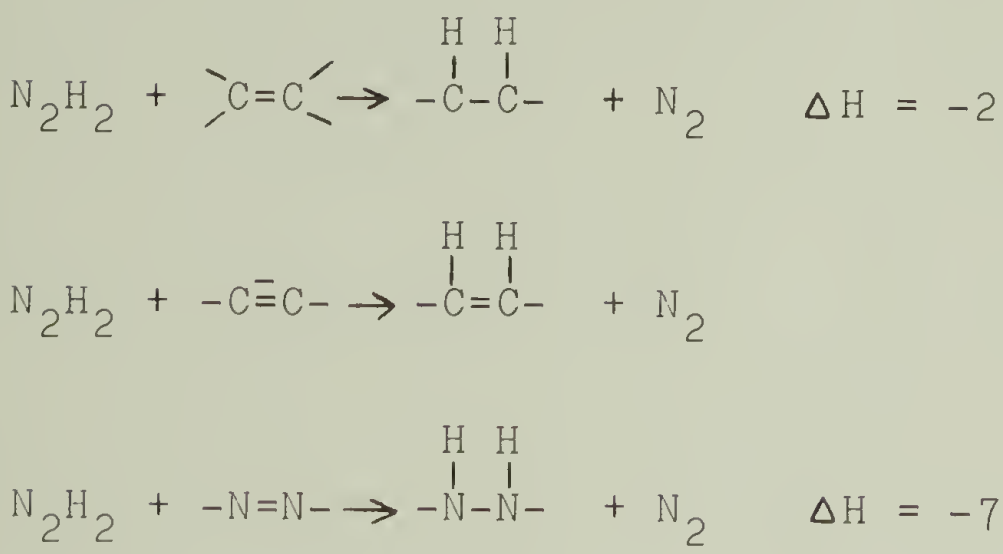
1. Planar $\quad H-N = N-H$

2. Zig-zag $\quad {}_{H}\diagup N = N \diagup^{H}$

A salient feature of this compound is its ability to undergo exothermic reactions with the non-polar carbon-carbon and nitrogen-nitrogen double bonds of olefins and

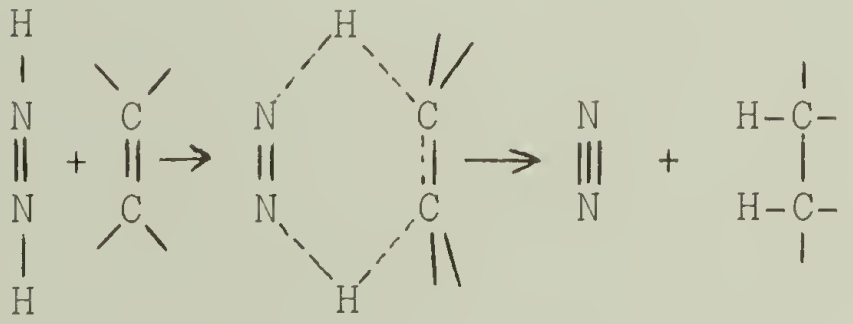
azo compounds as shown in Figure R 17.

FIGURE R 17. General Reactivity of Diimide.



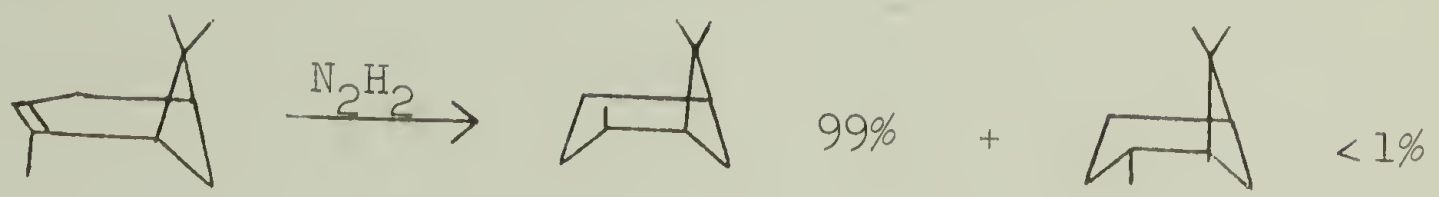
The presently accepted mechanism for diimide reduction is synchronous transport of hydrogen through a cyclic transition state (59, 60, 61) as illustrated in Figure R 18.

FIGURE R 18. Mechanism for Diimide Hydrogenation.



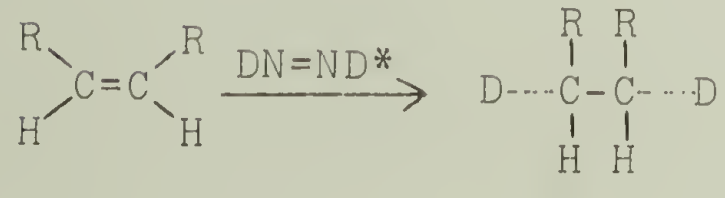
This cyclic transition state should and does form on the least hindered side of the olefin, even if the resulting product is the least thermodynamically stable of two possible products. Thus conversion of ∝-pinene leads to 99+% cis pinane, with the methyl group occurring in less

favored position (66). Mechanistic studies exist to sup-

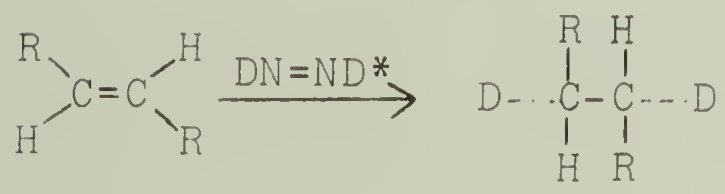


port this assignment. Reduction of <u>cis</u> and <u>trans</u> olefins by deutero diimide gives almost exclusively the <u>meso</u> and <u>dl</u> products respectively (59) (Figure R 19).

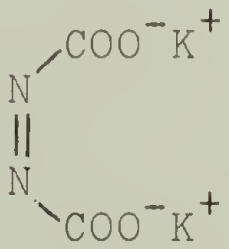
FIGURE R 19. Empirical Verification for Cyclic Transition States in Diimide Reduction.



<u>meso</u> (97%) R=CH_2OH; COOH

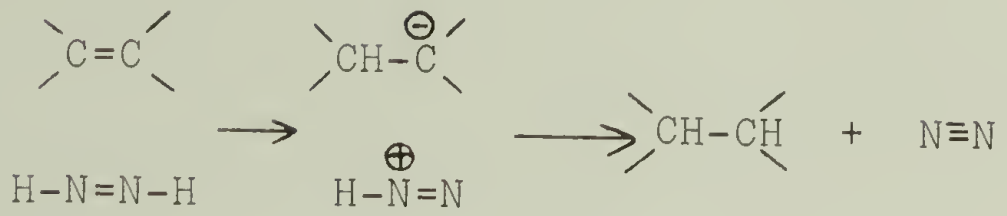


<u>dl</u> (97%) R=CH_2OH; COOH

*from  in D_2O

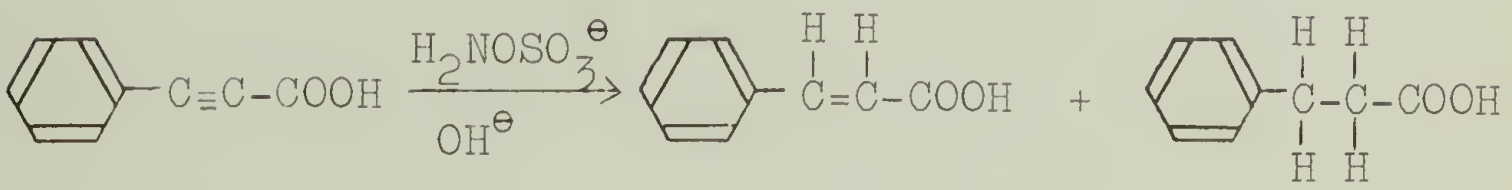
This behavior tends to exclude the alternate step-wise mechanism (59,61) suggested in Figure R 20.

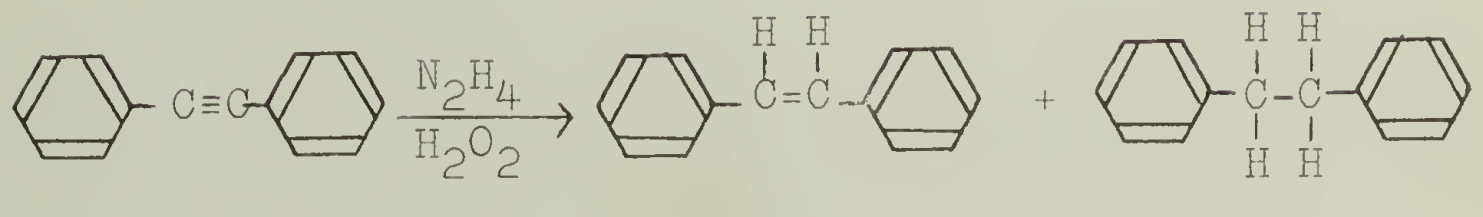
FIGURE R 20. Two-Step Mechanism for Diimide Reduction.



Also, substituted acetylenes are reduced exclusively to cis olefins (59, 61, 62) as shown in Figure R 21.

FIGURE R 21. Reduction of Acetylenes to Cis Olefins by Diimide.



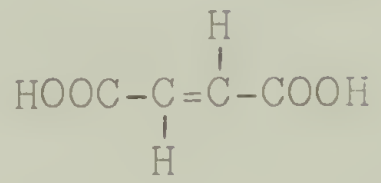
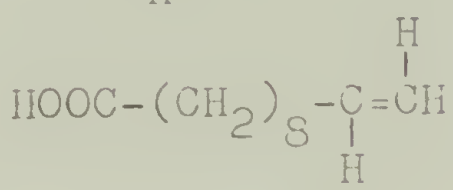
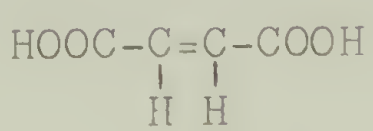
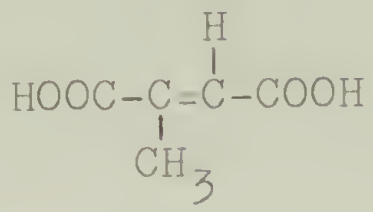
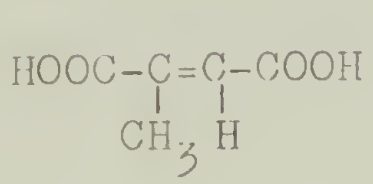


Conductometric studies (54) have shown that the reaction is non-ionic, while para substitution in cinnamic acid does not appreciably affect the hydrogenation rate of the double bond (see Table R 8, 7-11). This latter observation demonstrates that electronic interaction between the aromatic portion and the reaction center is weak, which is in accord with the weakly polar transition states occurring in a four-center mechanism (63).

The four-center mechanism provides the basis for several characteristic and important features of diimide reduction. Increasing substitution about the multiple bond should result in steric crowding in the transition state complex and adversely affect the reaction rate and conversion (see Table R 8: e.g., 1 vs. 4, 2 vs. 5, and 6 vs. 13 or 14). Experimentally it has been demonstrated that substituted acetylenes and mono- and di-substituted olefins are reduced in 70-90% yield, whereas tri-substituted olefins are reduced in yields of 20-40% under otherwise identical conditions (63,64).

TABLE R S

RATE OF REDUCTION* BY DIIMIDE AS A FUNCTION OF OLEFIN STRUCTURE (63)

Compound	Structure	% Hydrog. after Evolving 1 mole N_2H_2	Rel. Rate
1 fumaric		80	100
2 undecanoic		69	40
3 maleic		41	10
4 methylfumaric		18	3
5 methylmaleic		4	7

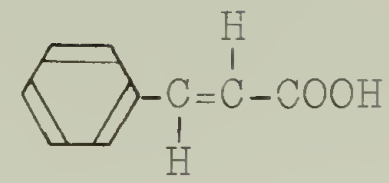
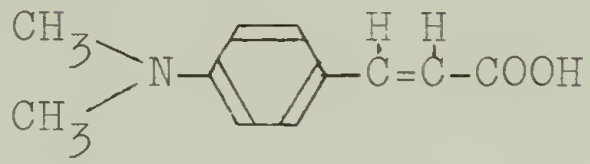
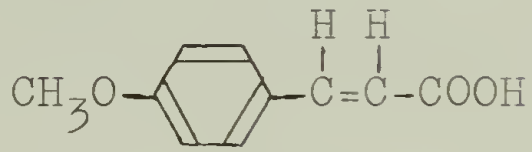
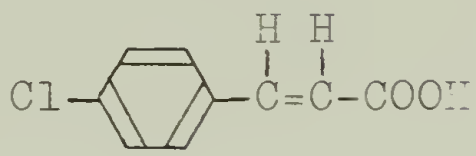
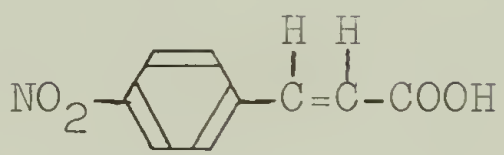
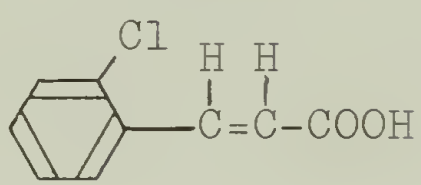
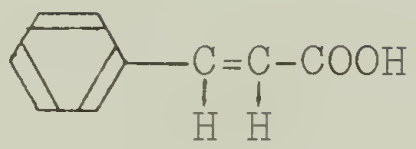
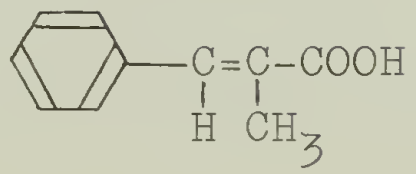
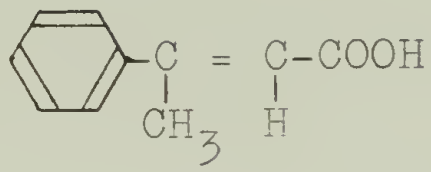
6	<u>trans</u>-cinnamic		41	10
7	<u>p</u>-dimethylaminocinnamic		32	8
8	<u>p</u>-methoxycinnamic		37	8
9	<u>p</u>-chlorocinnamic		37-39	8-9
10	<u>p</u>-nitrocinnamic		35-44	7-11
11	<u>o</u>-chlorocinnamic		44	11
12	<u>cis</u>-cinnamic		20	3
13	<u>α</u>-methylcinnamic		5	1.4

TABLE R 8--Continued

Compound	Structure	% Hydrog. after Evolving 1 mole N_2H_2	Rel. Rate
14 β-methylcinnamic		5	1.4

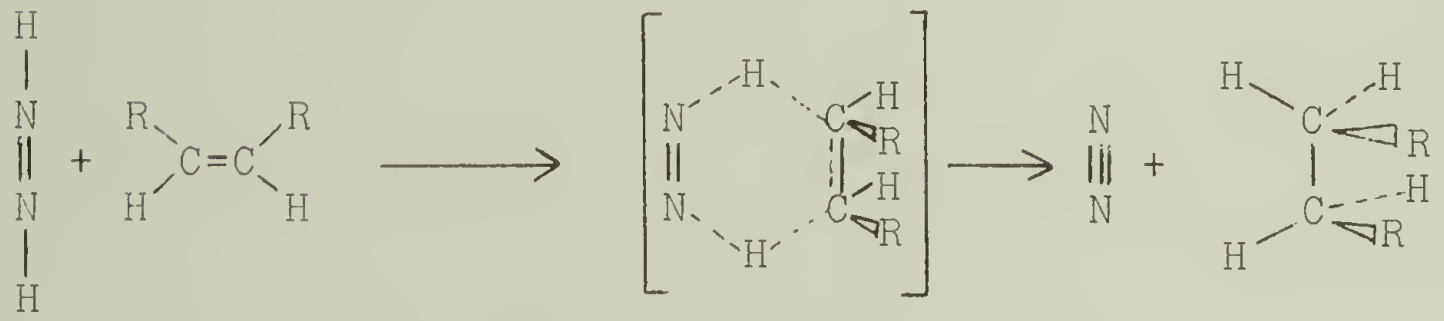
*Conditions: $N_2H_4 \cdot 2H_2O$ 36 m mole 100 m mole Ethanalamine

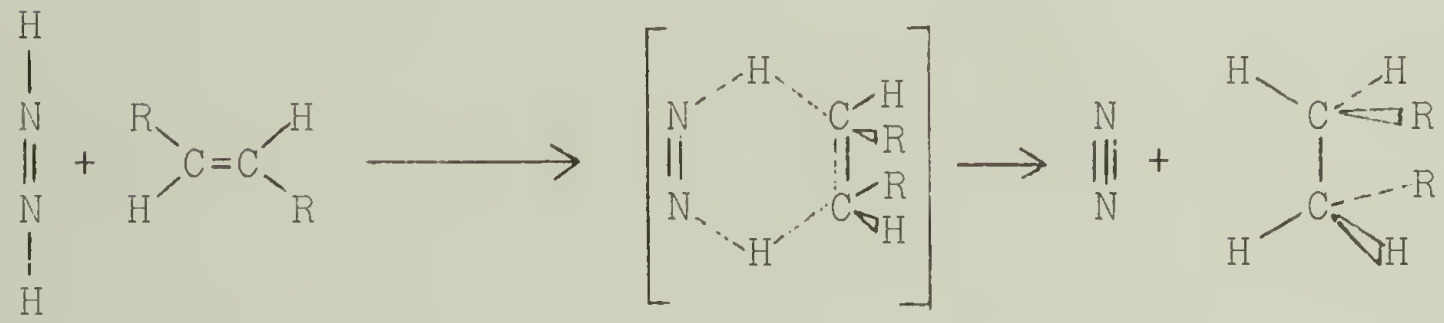
acids 6 m moles 100 ml water

25°C, Ph 10-11, 1 hour 40 ml·6N potassium ferricyanide

Related to this, the transition state for cis olefins should be more crowded than that for the corresponding trans olefin:

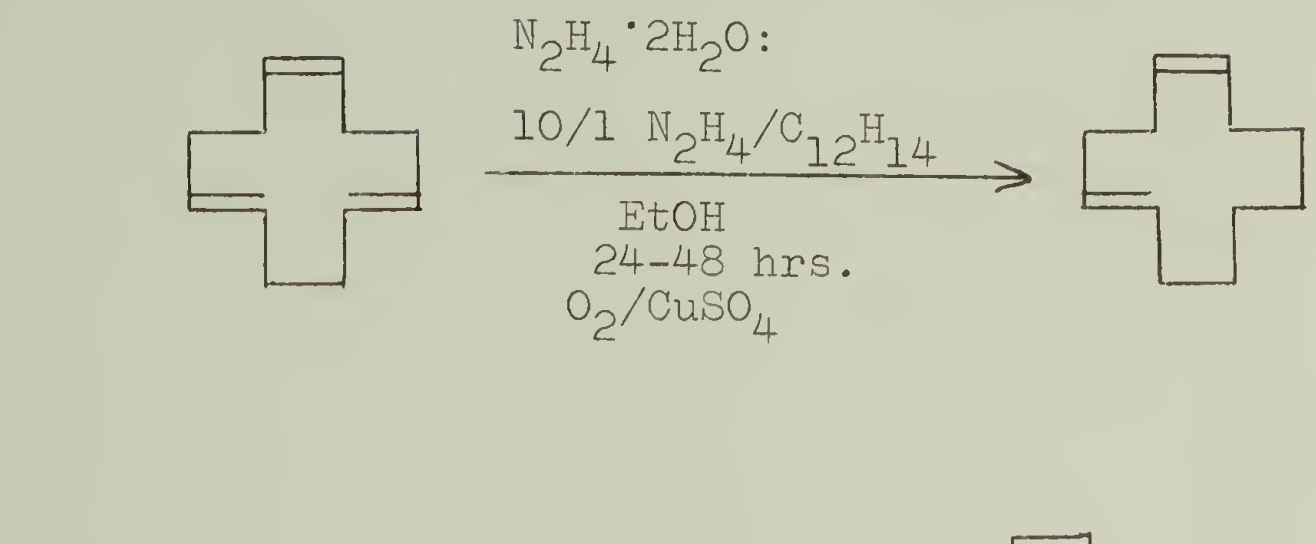
FIGURE R 22. Transition States for Cis and Trans Olefins in Diimide Hydrogenation.





Thus, trans double bonds should be hydrogenated more readily than cis (see Table R 8: 1 vs. 3 and 5 vs. 4, 6 vs. 12) double bonds. Similarly, the trans double bonds in cis, trans, trans-1,5, 9-cyclododecatriene (65), a cyclic internal olefin, are reported to be reduced completely before the cis linkage is attacked as shown in Figure R 23. These results are not general, however, since

FIGURE R 23. Selective Trans Reduction in 9-Cyclododecatriene with Diimide.



oleic acid (cis form) is hydrogenated slightly faster than elaidic acid, its trans isomer (54). Apparently, then, not only is the cis-trans nature of the diene important, but the adjacent structure and the conformation the molecule can assume also play a significant role. It may not be meaningful to generally discuss cis vs. trans hydrogenation rates when these are determined on the basis of a mixture of variously substituted alicyclic and cyclic olefins. In any case, the relative rate of cis vs. trans reduction is not, as yet, completely resolved.

The weakly polar four-center transition state may, however, account for the observed inertness to diimide of various polar double bonds and liable single bonds which

are otherwise reduced in catalytic hydrogenation. These structures include (6,12):

-C=O	-C≡N	$-NO_2$	-N=C-	-C-S-	-O-O-	S=O
ArI	ArBr	R-Br	R-SH	R-S-S-R	R-SCS-R	

A more polar, charge separated transition state requiring a relatively high activation energy for formation, is required for such polar bonds as indicated in Figure R 24.

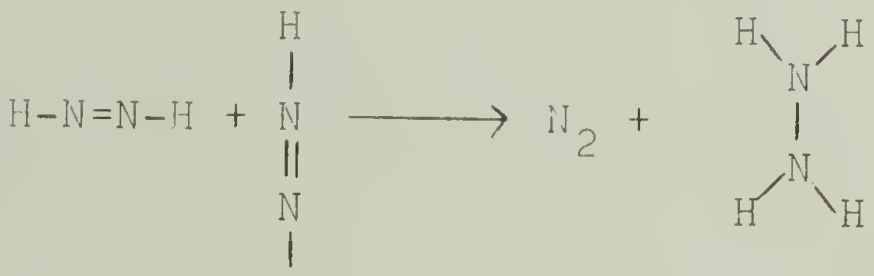
FIGURE R 24. Transition State in the Diimide Hydrogenation of Polar Multiple Bonds.

Thus, instead of reduction, the self-disproportionation of diimide (see later discussion) becomes relatively more favored and little reaction occurs. Other entities which are inert to diimide include aromatic nucleii; however, conjugated dienes such as cyclopentadiene are reduced (61,64). Concerning bond polarity, it is interesting to note that α,β-unsaturated carbonyl compounds are reduced with great difficulty, but when the multiple bond is

symmetrically flanked on both sides by the same polar groups, reduction proceeds readily (59,66).

The reactivity of diimide with azo compounds allows the reagent to act as both a hydrogen donor and acceptor. Thus, self-disproportionation of diimide is the main side reaction and principal shortcoming of these reductions as depicted in Figure R 25.

FIGURE R 25. Disproportionation of Diimide.



One might conjecture that the seriousness of this side reaction depends primarily on the relative reactivity of the unsaturated substrate, and the amount of free diimide present in solution at any given time. Substrates which are non-polar and are not sterically encumbered have a greater probability of reacting with diimide before it self-disproportionates. Alternatively, if the diimide precursor and reaction conditions are such that most of the diimide is generated within a short time span, then the amount of free diimide potentially present in solution is maximized. Since the disproportionation is a bimolecular

process, it should become relatively more important under these circumstances. The quantitative aspects of such a problem (Table R 9) have been studied for the case of diimide generated in the thermal decomposition of benzenesulfonylhydrazide (55, p 376) (see later discussion). This example is of particular importance here since a closely related compound, p-toluenesulfonylhydrazide, was used as the diimide source in the present work. The effect of the nitro group is to greatly assist in the decomposition of the hydrazide to diimide, which is in accord with the electron withdrawing properties of this substitutent. The temperature required for decomposition is greatly reduced, while the amount of reagent lost through disproportionation is considerably enhanced. As indicated by the graph, increasing the substrate to hydrazide ratio has the anticipated effect of lessening the relative importance of self-disproportionation.

In addition to disproportionation, diimide has also been shown to undergo a base induced decomposition to nitrogen and hydrogen. This process occurs concurrently and in competition with the disproportionation reaction (55, 277). As indicated by the data in Table R 10, increasing the amount of base used to facilitate diimide formation causes the relative amount of decomposition

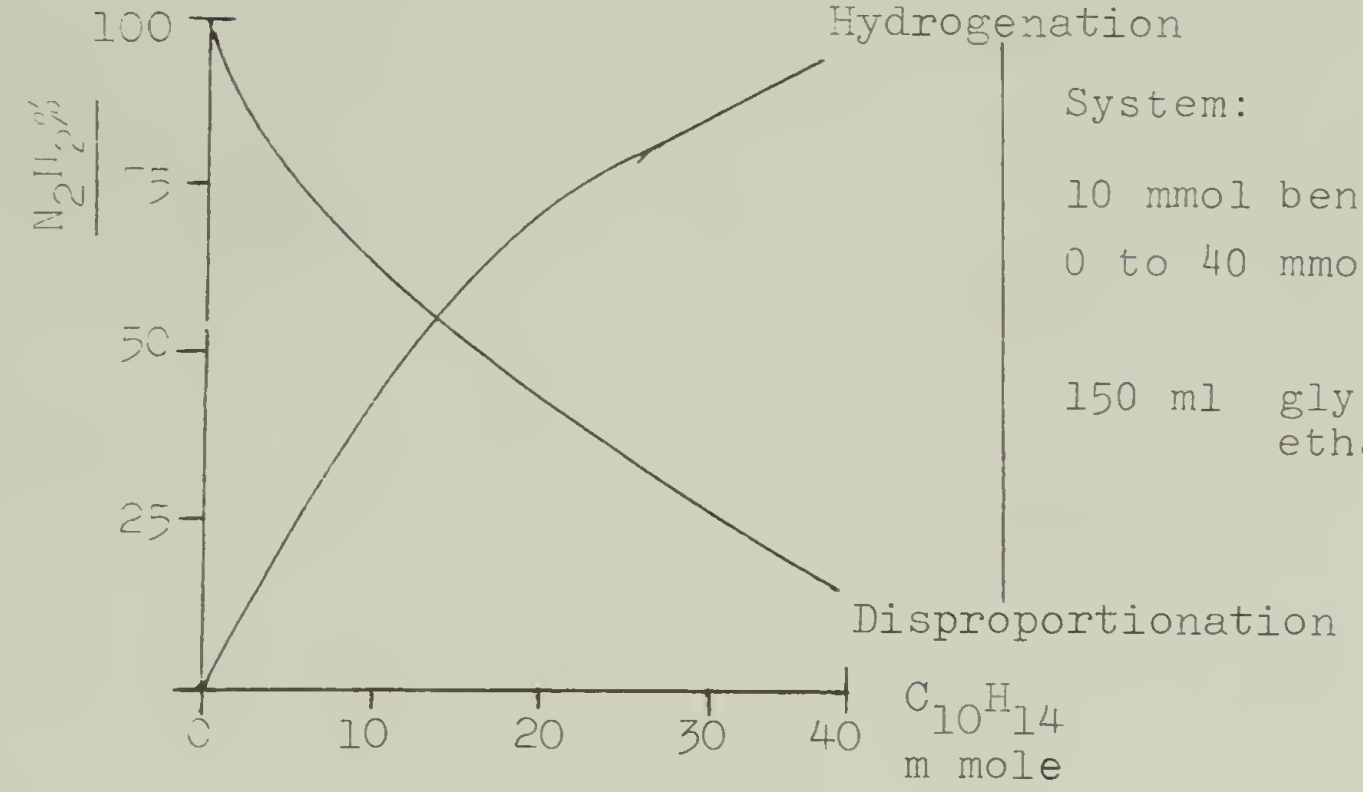
TABLE R 9

SUBSTITUTENT EFFECTS OF THE PERCENTAGE OF HYDROGENATION VS. DISPROPORTIONATION IN DIIMIDE REDUCTION

Diimide Source	Temperature (°C)	% Disproportionation	% Hydrogenation
$\text{ØSO}_2\text{NHNH}_2$	104.9	55 ± 2	45 ± 2
$\underline{m}\text{NO}_2\text{ØSO}_2\text{NHNH}_2$	78.8	69	31
$\underline{o}\text{NO}_2\text{ØSO}_2\text{NHNH}_2$	39.1	97	3

System: 5 mmol benzenesulfonylhydrazide
5 mmol dihydrodicyclopentadiene ($C_{10}H_{14}$)
60 ml glycol monomethylether-ethanolamine (.91M)

FIGURE R 26. Effect of Hydrazide to Substrate Ratio on the Competition Between Hydrogenation and Disproportionation.



System:

10 mmol benzenesulfonylhydrazide

0 to 40 mmol dihydrodicyclopentadiene
$C_{10}H_{14}$

150 ml glycol monomethylether/ethanolamine (.91M)

TABLE R 10

DISPROPORTIONATION VS. DECOMPOSITION IN THE BASE CATALYZED CLEAVAGE OF p-BENZENESULFONYLHYDRAZIDE

KOH moles/l (initially)	% Disproportionation*	% Decomposition
2.0	3	97
0.51	33	67
0.25	63	37
0.10	92	8
0.06	99	1

Decomposition $N_2H_2 \longrightarrow N_2 + H_2$

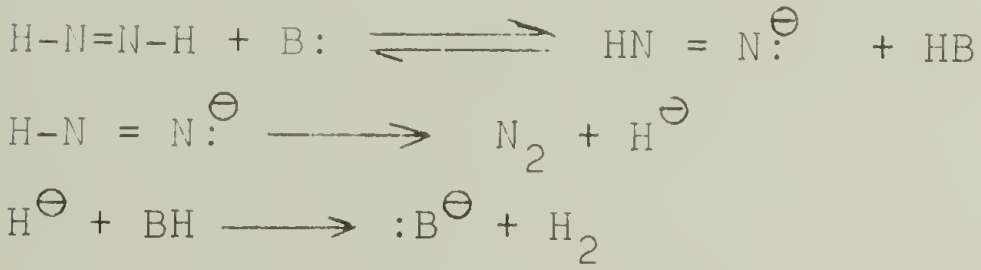
Disproportionation $N_2H_2 \longrightarrow 1/2N_2H_4 + 1/2N_2$

Analysis: Based on amounts of N_2, H_2 and N_2H_4 formed in the base catalyzed cleavage of 10 mmole of benzenesulfonylhydrazide on 165 ml of glycol monomethylether at 99°C.

to nitrogen and hydrogen to increase. Thus, it has been suggested that this decomposition occurs by way of diimine anions (Figure R 27a) formed from the action of the base on free diimide. The alternate possibility of decomposition occurring directly from the hydrazide anion (Figure R 27b) could be ruled out since the amount of decomposition vs. disproportionation of N,N'-bis (methoxy-carbonyl) anthracene-9,10-bisimine, from which the hydrazide anion cannot be formed, was proportional to the amount of potassium hydroxide present (55; p 278) in a similar set of experiments. In the particular case of

FIGURE R 27. Mechanisms for Diimide Decomposition.

a. Diimide Decomposition by Diimine Anions.



b. Decomposition from the Dydrazide Anion.

sulfonylhydrazides of interest here, this undesirable side reaction may be completely suppressed either by using

ethanolamine as the base or by depending upon thermal decomposition alone (i.e., no base) to generate the diimide.

There are two final features of diimide reduction which are in sharp contrast to catalytic reduction and may be advantageous for the application of this method to polymer systems. First, when the reduction is performed step-wise no migration or cis/trans isomerization of double bonds occurs as in some catalytic processes (54). Secondly, the presence of sulfur appears not to effect the reducing ability of diimide. In the classic example, allyl disulfide was reduced to n-propyl disulfide, a reduction which cannot be performed by catalytic hydrogenation (60) (Figure R 28).

FIGURE R 28. Reduction of Allyl Disulfide with Diimide.

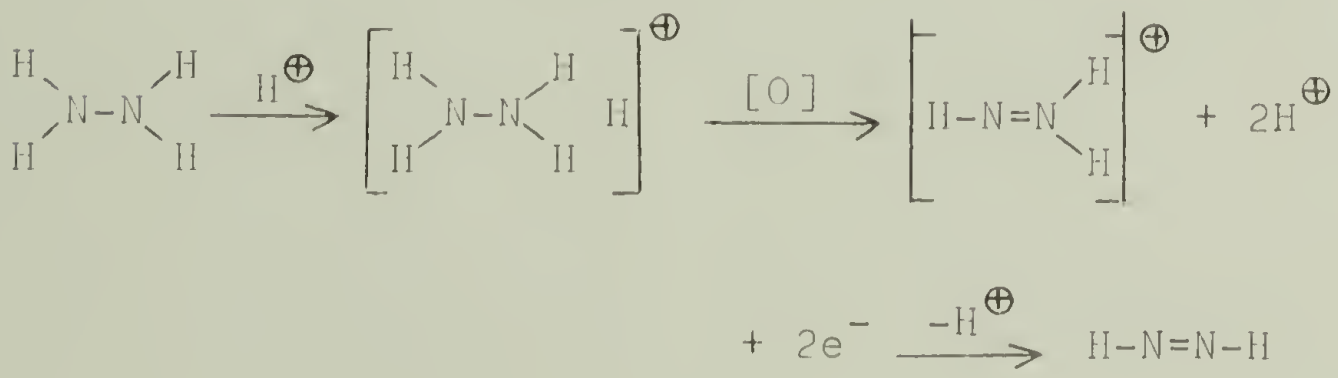
$$CH_2{=}CH{-}CH_2{-}S{-}S{-}CH_2{-}CH{=}CH_2 \xrightarrow[p\text{-}TSH]{N_2H_2} CH_3CH_2CH_2{-}S{-}S{-}CH_2CH_2CH_3$$

The instability of diimide at useful temperatures requires that the reagent be generated in situ, normally by the decomposition of some precursor material. There are several possibilities, and the eventual choice depends upon the particular solubility and temperature

requirements of the system under investigation.

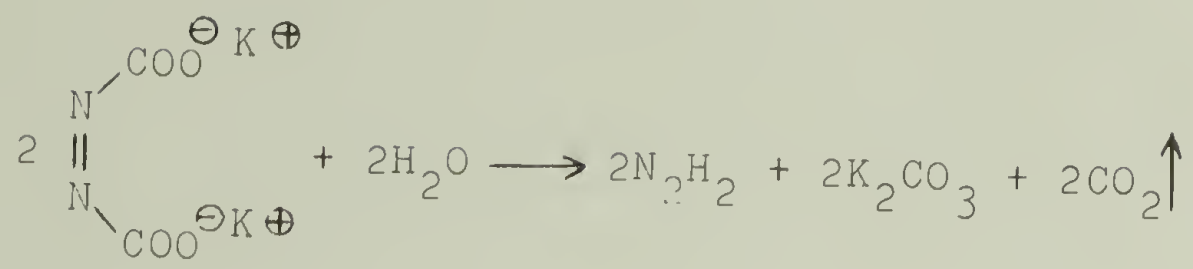
Diimide may be generated from hydrazine in aqueous and alcoholic solutions in the presence of oxygen or suitable oxidizing reagents (air, potassium periodate, hydrogen peroxide, etc.) and preferably in the pH range 8.5 to 9.0. Suitable solvents include methanol, ethanol and higher alcohols, or the methyl and ethyl celloxolves. Hydrazine to olefin ratios of at least two are required, and the most suitable reaction temperature is about 50°C, a temperature which allows good reaction rates but which avoids extensive olefin oligiomerization. The acid-catalyzed scheme illustrated in Figure R 29 has been proposed (54).

FIGURE R 29. Generation of Diimide from Hydrazine.



Diimide also results from the thermal decomposition of potassium azodicarboxyate salts in warm aqueous solution (67,68), as follows:

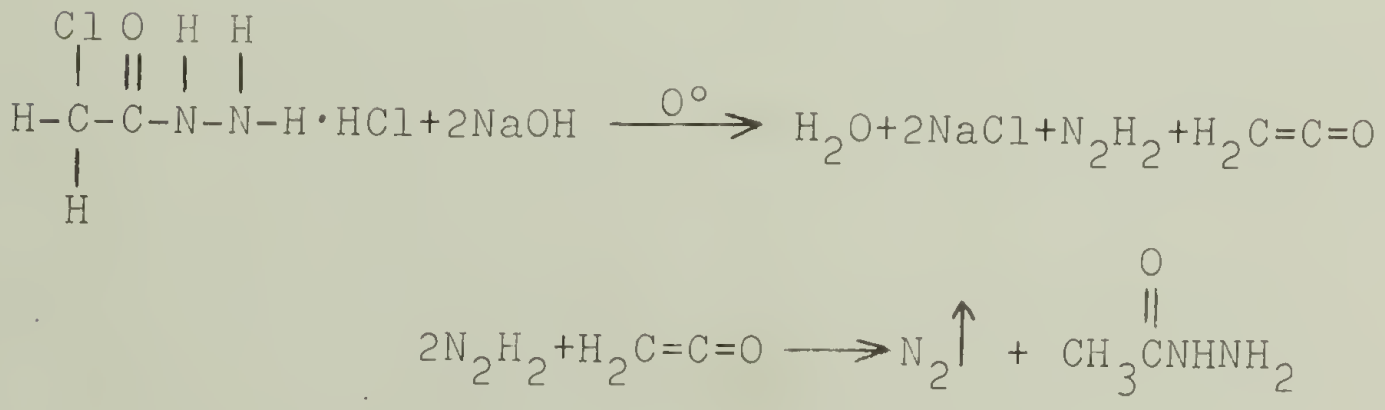
FIGURE R 30. Generation of Diimide from Azodicarboxylates.



When the diimide is generated in the presence of olefins such as maleic and fumaric acids, cyclohexene and allyl alcohol, reduction occurs (55, 61, 69).

Diimide may be generated at a relatively low temperature, 0°C (70), by the decomposition of chloroacetylhydrazine in aqueous alkali. The decomposition is instantaneous and complete; in the absence of olefin the diimide and ketene quickly react to form acetylhydrazine which is stable and inert under these conditions.

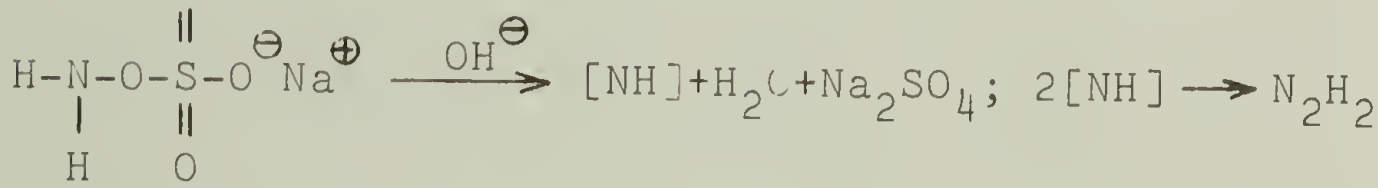
FIGURE R 31. Generation of Diimide from Chloracetylhydrazine.



For example, using a stiochimetric amount of chloroacetyl-hydrazide to olefin, azobenzene is quantitatively reduced, and allyl alcohol is converted in 70% yield into propanol.

Diimide has been postulated to form in an indirect manner by the dimerization of "nitrene," a transient intermediate thought to occur in the alkaline decomposition of chloramine and hydroxylamine-O-sulfonic acid (62, 71, 72) as shown in Figure R 32. Such reagents were shown to

FIGURE R 32. Generation of Diimide from Chloramine or Hydroxylamine-O-Sulfonic Acid.

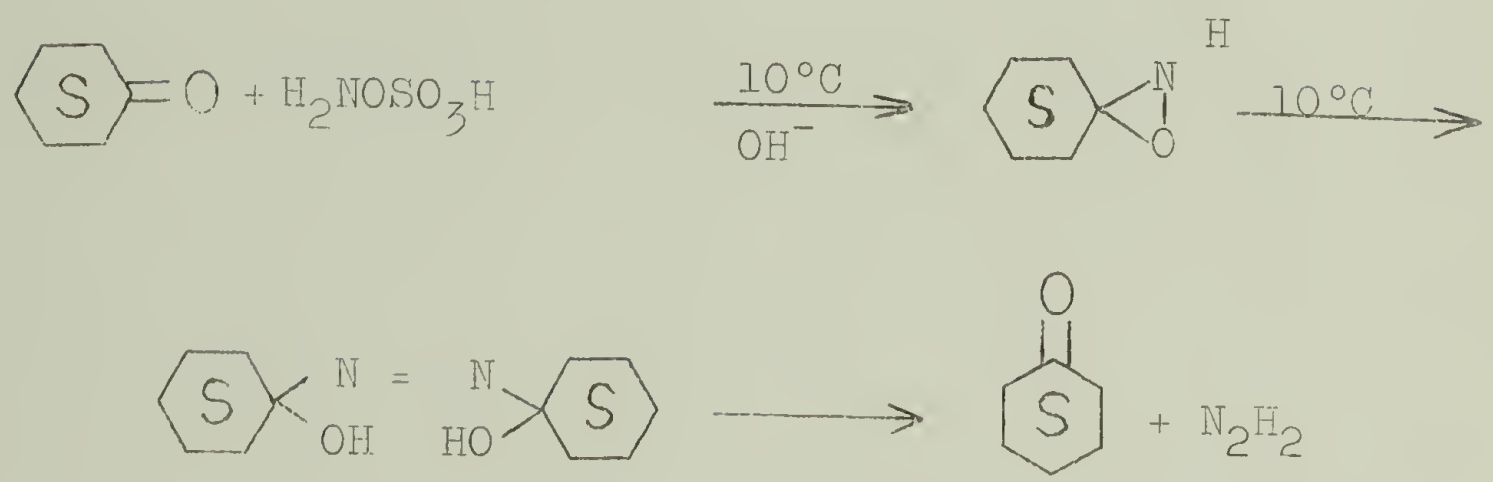


reduce cyclohexene, ethylene, cinnamic and maleic acids in 30 to 50% yield in aqueous or methanolic alkali.

Alternately, using hydroxylamine-O-sulfonic acid diimide may be generated by a more indirect route. This compound may be reacted with cyclohexanone to give an adduct that dimerizes into 1,1-dihydroxy-azocyclohexane at 10°C. This crystalline product, when heated to room temperature decomposes into diimide and cyclohexanone

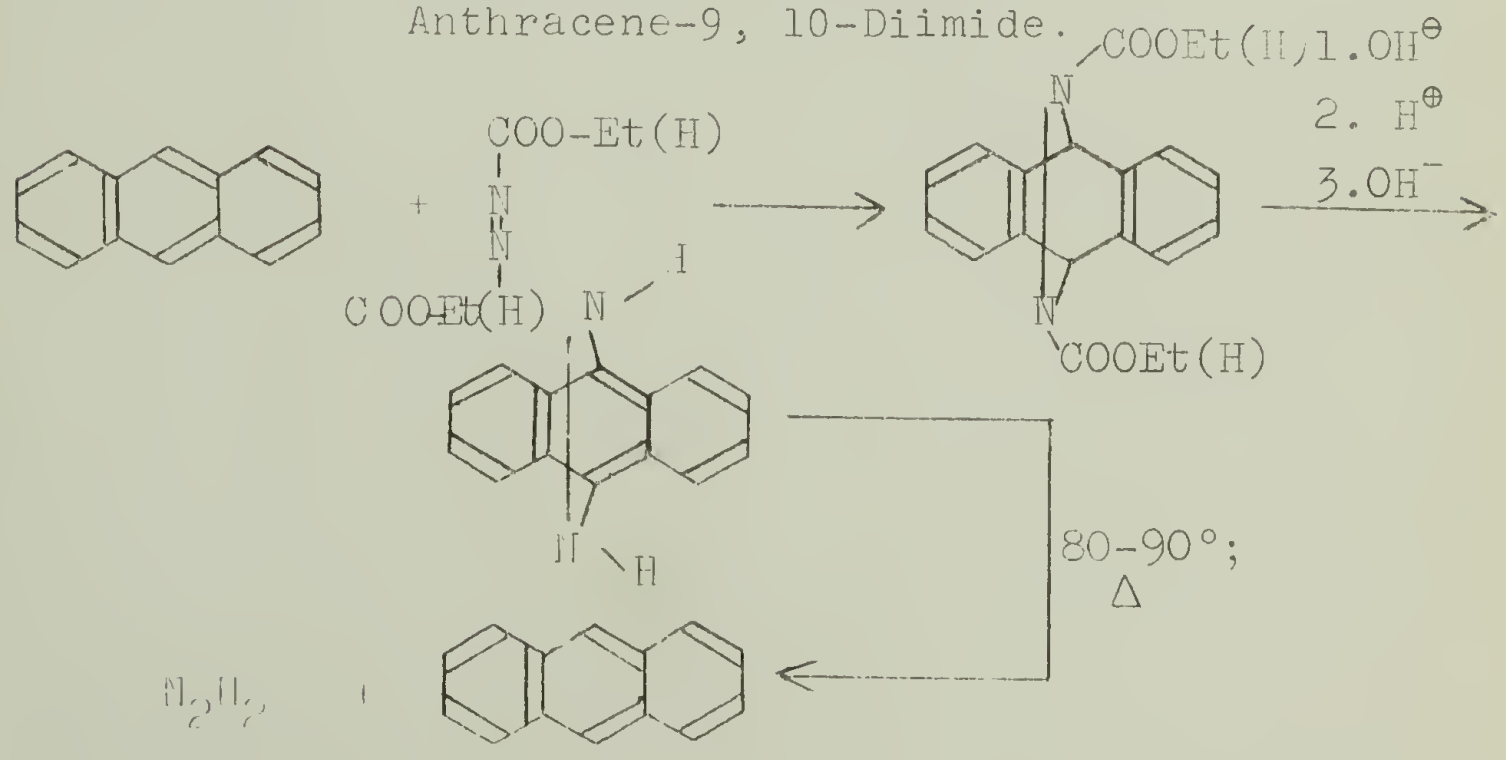
(76,77) as shown in Figure R 33.

FIGURE R 33. Generation of Diimide from 1,1-Dihydroxy-azocyclohexane.



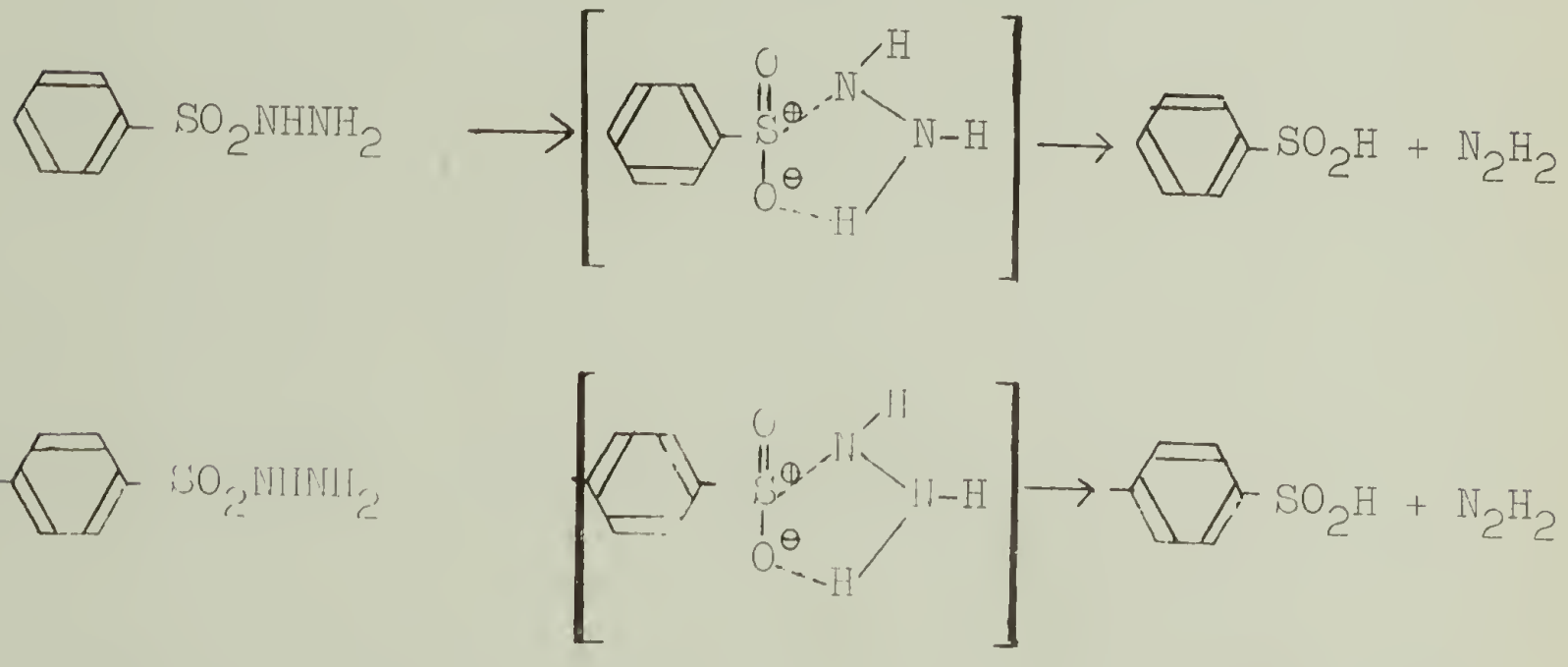
Diimide can be generated without recourse to acidic or basic media. One such method is the thermal decomposition of the diimide anthracene adduct, anthracene-9, 10-diimide (73) illustrated in Figure R 34.

FIGURE R 34. Generation of Diimide from Anthracene-9, 10-Diimide.



Also, certain aryl and acyl hydrazides, in particular benzene-and toluenesulfonylhydrazide (61,74) may be thermally decomposed to diimide and the corresponding acid (Figure R 35). Since these reagents were utilized in this

FIGURE R 35. Generation of Diimide from Arylsulfonylhydrazides.



present work, their chemistry is reviewed in more detail. Decomposition of aryl hydrazides occurs normally at temperatures around 100°C and higher. However, diimide may be generated with these reagents at rates suitable for synthesis at temperatures as low as 25° by addition of ortho, meta or para-NO_2 groups onto the aromatic ring of the aryl hydrazide (meta, 75°; para, 50°; ortho, 25°) (7, p 273). Hydrazide to olefin ratios of two are normally used, and reaction times are from one to four hours at solvent reflux, under nitrogen. The decomposition may occur with or without added bases such as hydroxyl ion or organic

amines (e.g., ethanolamine). These bases, and more polar solvents like dimethylformamide (see below and next section), have the general effect of lowering the activation energy required for diimide generation, presumably by stabilizing the polarization which occurs in the cyclic transition state. In turn, this lower activation energy for decomposition accelerates the rate of diimide formation. Some relevant kinetic and thermodynamic constants are available for the thermal decomposition of the benzenesulfonylhydrazide system (Table R 11; 55); note especially the ΔS values consistent with a cyclic transition state and how these are lowered by added bases reflecting a more ordered intermediate state.

Initial decomposition of the hydrazide yields the diimide and a arylsulfinic acid. If basic acceptors (ethanolamine) are present in solution, reaction sequences involving the acid terminate here. Otherwise, a series of complex, intertwined reactions are thought to occur (55) as given in Figure R 36.

Fortuitously, all the products are either inert gases, ionic materials, or exhibit good methanol solubility. These characteristics should be useful properties when applying the reaction to polymeric substrates. On the other hand, the sulfonic acid initially formed is potentially capable

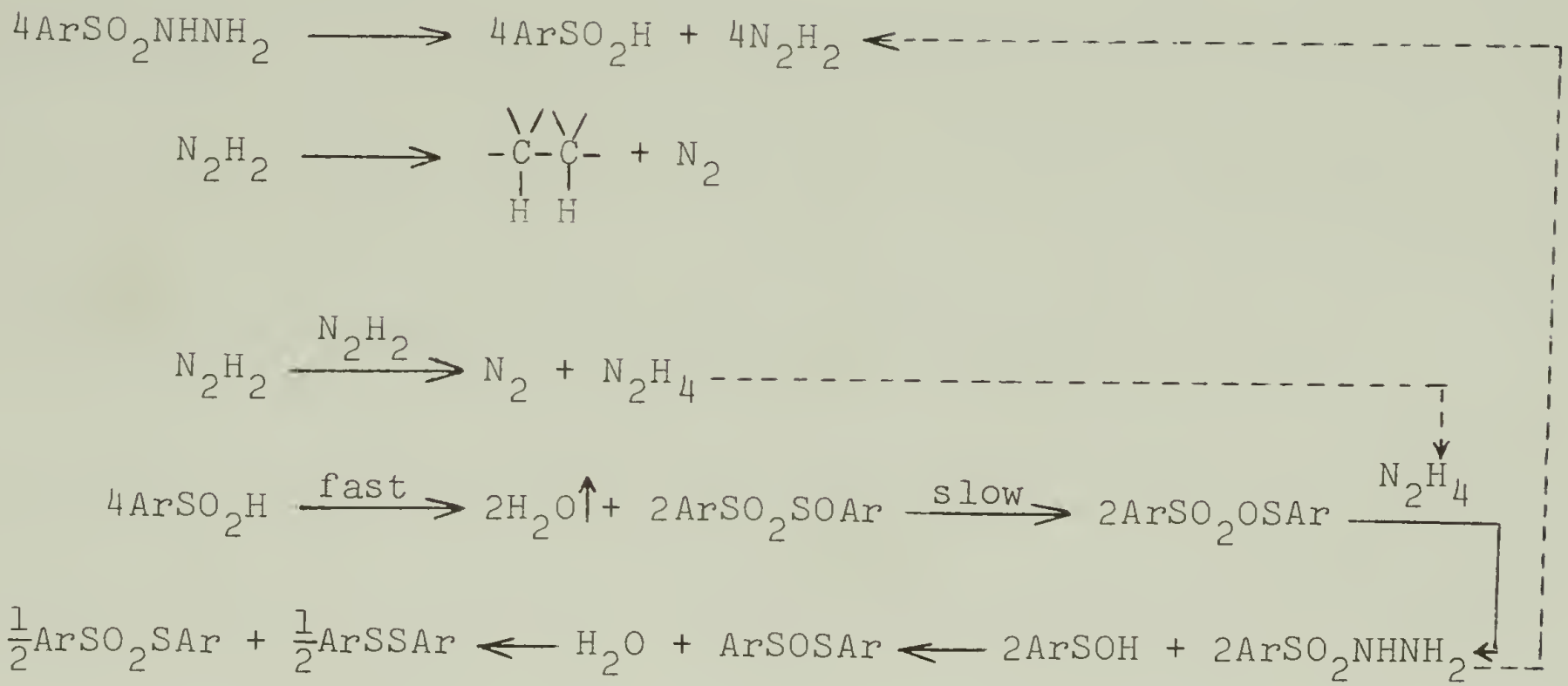
TABLE R 11

THERMAL DECOMPOSITION OF BENZENESULFONYLHYDRAZIDE-KINETIC AND THERMODYNAMIC PARAMETERS

Base	T(°K)	k_{decomp}^{x} $10^2(min^{-1})$	E_a	ΔH (Kcal/mole)	ΔG	ΔS (cal/deg-mole)
0.91M	352.0	0.71	23.5	22.8	27.0	-12.0
ethanolamine	372.3	4.4			27.3	-12.2
none	372.3	1.94	20.9	20.1	27.9	-21.0
	392.4	8.26			28.3	-20.9

System: 10 mmol benzenesulfonylhydrazide
165 ml glycolmonomethyl ether

FIGURE R 36. By-Products Formed in the Decomposition of p-toluenesulfonylhydrazide.



of cationically crosslinking or cyclicizing a partially hydrogenated diene polymer. Further, the aryl disulfide by-product contains a potentially reactive sulfur-sulfur linkage which could be the source of an undesirable side-reaction. However, it has been reported that hydrogenation of various low molecular weight olefins with sulfonyl hydrazides results in no sulfur containing by-products (55, p 278).

VI. Use of Diimide with Polymeric Substrates

Only one example involving the use of diimide to reduce polymeric substrates has been reported (75). Diimide was evaluated as a reagent to remove the residual unsaturation in commercial poly (vinyl chloride), caused by loss of hydrogen chloride, and to retard redevelopment of unsaturation. Since the reaction was carried out to regenerate the original polymer structure, minus the small amount of chlorine lost, there does not appear to be any reported work which uses diimide to convert fully unsaturated precursor polymers (i.e., diene polymers such as polybutadiene or polyisoprene) into saturated derived polymers.

Reduction of unsaturated poly(vinyl chlorides) was found to require solvents which boiled above 100°C, and

which dissolved both the polymer and the hydrazide. The best solvent of those examined was ortho-dichlorobenzene; dimethylformamide and hexamethylphosphoramide, while useful, were found less suitable.

In general the reactions were carried out at 100°C for four hours. The most favorable ratio of hydrazide to polymer (mer-basis) was .25. Typically, a sample treated for six hours in o-dichlorobenzene had .58 C=C/100 monomer units initially and had this value reduced to .15/100, corresponding to a 75% removal of residual unsaturation. The intrinsic viscosities of this sample were evaluated in cyclohexanone at 30°C before and after reaction. The values of .692 found before reaction and .697 found after treatment illustrates that the para-toluenesulfonylhydrazide method apparently does not cause crosslinking for degradation in this particular system. Clearly, this is an important preliminary consideration in using this material for polymer modification reactions.

EXPERIMENTAL

I. General Techniques

A. Analytical instrumentation. Infrared spectroscopy. Infrared spectroscopic analyses (Appendix 3) were performed with the Perkin-Elmer model 257 double-beam recording spectrophotometer. Liquid samples were run neat, while polymeric materials were analyzed in carbon disulfide solution (compensated against pure carbon disulfide) or as films cast onto sodium chloride plates from various solvents. The region from 4000 cm^{-1} to 625 cm^{-1} was scanned at medium scan speed (12 min per scan) or in a few instances at slow scan speed (24 min per scan). All spectra were run at room temperature, using a 0.05 mm thick polystyrene film as a wavelength standard.

Ultraviolet spectroscopy. Ultraviolet spectra were determined using the Carey 505 U.V.-Visible double-beam recording instrument at a 2.5 Å/sec scan speed. Sample solution, and reference (solvent) holders were 1 cm path-length quartz cells (Fisher). The polycyclohexadienes were run in tetrahydrofuran solution and polycyclohexanes in cyclohexane solution. The spectra were scanned from 220 mu to 300 mu.

Nmr spectroscopy. Nmr spectra were run on the Varian A-60 or A-60A 60 MHz instruments at 37°C probe temperature, 0-500 cps sweep width, and 500 sec sweep time. Other

important analytical parameters are indicated with specific spectra.

Membrane osmometry. Samples having molecular weights (number average) over 40,000 had their number average molecular weights determined with a Hewlett-Packard membrane osomometer using chloroform or benzene as solvents at 37°C.

Vapor phase osmometry. The number average molecular weights of samples having molecular weights under 25,000 were determined on the F/M (Hewlett-Packard Co.) model 300 vapor phase osmometer at 50°C in benzene or cyclohexane, using benzil as the standard.

Differential scanning calorimetry (DSC). Melting ranges and the glass transition behavior of polymer samples were determined with the Perkin-Elmer DSC-1B machine. Liquid nitrogen coolant was used to obtain thermograms down to -70°C; ice-water coolant was used for thermograms down to +5°C; no coolent was required for curves starting at +35°C or higher. Upper temperature limits were generally less than +300°C. Heating rates are indicated with particular thermograms in Appendix 6.

Fisher-Johns softening point device (Fisher Scientific Co.). The instrument is essentially an optical hot stage of aluminum designed to accommodate two 18 mm

circular cover discs, between which a few tenth's milligram of a powdered sample may be inserted. The stage can be heated up to +300°C at various rates to observe transitions which are visually apparent (e.g., melting points). Reproducibility is claimed to be ±0.5°C, with an accuracy of 1-2°C without calibration standards for materials which exhibit well defined melting points.

Gas chromatography. Gas chromatographic separations and analysis were performed with the Varian model 1520 auto preparative gas chromatograph equipped with a matrix temperature programmer. Gas chromatography curves are collected into Appendix 5.

Two basic sets of instrumental conditions were used. (a) Analysis and purification of 1,3-CHD: column, 20 ft x 3/8 inch tetracyanoethylatedpentaerythritol (TCEPE) on a 50/60 mesh Anaprep support at 90-100°C; injector, 120-140°C; Thermal Conductivity detector, 120-150°C at 150 ma; carrier, helium gas at 125 cc/min; sample sizes, up to 150 µl. (b) Analysis and purification of dimethylcyclohexanols, dimethylcyclohexylacetates, and dimethylcyclohexenes: column, 20 ft x 3/8 inch SE-30 (silicone) on a ABS support; injector, 215°C; Thermal Conductivity detector, 237°C at 150 ma; carrier, helium at 125 cc/min; sample sizes, up to 100 µl; column temperatures for

cyclohexanols, 160°C; cyclohexylacetates, 187°C; and cyclohexenes, 110°C.

B. Research services (Office of Research Services, University of Massachusetts). Glassblowing. Drawings and specifications for the major pieces of equipment custom made at the glass shop and used in this investigation are collected into Appendix 2.

Microanalytical analysis. All the elemental analysis and molecular-weight determinations were preformed by the microanalytical laboratory which also provided general assistance and advice on the operation of the gas chromatograph.

C. Solvents, reagents, and monomers. A compilation of the principal reagents, solvents and chemicals and their sources has been collected into Appendix 1. Solvents were used as received unless preceded by the word "purified." In this latter case, solvents boiling at less than 100°C were refluxed under a nitrogen blanket and over potassium metal for 12 to 24 hours, and distilled under nitrogen. The center 60 to 75% was retained by distilling directly into brown bottles which had previously been cleaned, heated to 120°C, purged with nitrogen and capped. Each bottle contained a small amount of molecular sieve (Linde 6A) which had been previously washed several times with solvent and heated with the bottle during the drying

procedure. Solvents boiling at greater than 100°C were prepared similarly, except that sodium metal was used for the reflux operation. Several additional reagents and two monomers were also purified after receipt. The purification procedures for these latter materials are given here.

Para-toluenesulfonylhydrazide (p-TSH). A saturated solution was prepared using hot (60°C) 95% ethanol, vacuum filtered hot, and the filtrate allowed to cool. White, needle-like crystals readily formed which were isolated by vacuum filtration (85 to 90% recovery) and dried by treatment in a vacuum oven (1-5 mm) at 40°C for 6-8 hours. The final product was transferred into brown bottles and stored under nitrogen until use.

Tetramethylethylenediamine (TMEDA). 50 mls of TMEDA were refluxed under nitrogen and over calcium hydride, distilled, and the center 60% retained in a stoppered receiver flask, under nitrogen, until use.

2,5-Dimethyl-2,4-hexadiene. This monomer was purified according to the procedure suggested in Macromolecular Synthesis (78). The liquid monomer (m.p., +14°C) was incompletely frozen in a covered beaker by cooling with a surrounding ice-water bath. The unfrozen core (some 10-20%) was decanted and the remainder remelted. This process was repeated once more. The final product was

distilled and collected under nitrogen (b.p., observed, +137°C) for immediate use.

1,3-CHD. (a) Purification. The monomer was supplied in brown, air tight bottles in greater than 99% purity by the Columbia Organics Chemical Co. For general storage, the bottle was opened, flushed with prepure nitrogen from a tank source, and prewashed and dried molecular sieves (Linde 6A) were added. For this purpose fresh sieves were washed twice by contact with purified tetrahydrofuran, dried 12 hours at 120°C and stored in a clean, closed container under nitrogen. The sample was recapped and retained in the refrigerator until use. For final purification, a portion of the sample was transferred by syringe into a rigorously preflammed, nitrogen filled vacuum bulb containing a Teflon stir bar and n-butyllithium initiator from which the solvent had previously been removed under vacuum. About 0.25 to 1.0 ml of 1.6 or 2.25 M n-butyllithium in hexane solution per 5 ml of monomer was usually sufficient. The solution was stirred until initiation was apparent (solution turns green to yellow green), then the monomer was immediately vacuum distilled into the reaction pot which had been attached to an adjacent position on the vacuum distillation manifold (Figure 2, Appendix 2). For the study involving the

determination of polymerization reaction byproducts, removal of residual cyclohexene and benzene was accomplished by a preparative gas chromatographic technique. General instrument settings and columns have been noted previously. The gas chromatograph was operated in automatic injection (200 ul per injection) and collection modes with collection occurring under helium. Three preparative runs were performed. Analysis of the products after separation indicated complete benzene removal (detection limits, less than 1/10,000) and 80 to 90% removal of cyclohexene on the basis of peak areas before and after separation (Appendix 5; GC-1,2). (b) Analysis of the type and quantity of impurities in 1,3-CHD. The series of samples given in Table E1 were injected onto the gas chromatograph. Absolute and relative retention times (defined as the time necessary to detect the maximum rate of elution of a component) of known (GC-4) vs. unknown impurity (GC-1) peaks were compared to verify the identity of the impurities present (see Table E2). To determine the amount of each material quantitatively, the peak areas of cyclohexene, 1,3-CHD, and benzene were found by plainimeter for sample 2 where the mole fraction of each component present was known. This allowed calculation of relative response factors. Using these, and the measured areas of

TABLE E1

SAMPLES AND INSTRUMENTAL CONDITIONS FOR THE ANALYSIS OF IMPURITIES IN 1,3-CHD

	Sample Composition	Size Injected	Temperature Settings		
			Col.	Inj.	Det.
1.	1,3-CHD (fresh sample)	150 ul	92.5	130	128
2.	1,3-CHD/benzene/cyclohexene				
	compound — Wt (g) corrected — mole % corrected				
	1,3-CHD — 0.8394 — 0.745				
	cyclohexene — 0.1455 — 0.128				
	benzene — 0.1339 — 0.127				
3.	air only	10 ul	92.5	130	128
4.	1,3-CHD + .1% by volume cyclohexene benzene 1,4-CHD	150 ul	92.5	132.5	124
5.	1,3-CHD 2 parts by volume with cyclohexane 1 part by volume	150 ul	90	130	122.5

TABLE E2

OBSERVED RETENTION TIMES OF 1,3-CHD AND ITS PRINCIPAL CONTAMINENTS

Sample	Absolute Retention Time(mm)* RT_a						Relative Retention Times(mm)** RT_r					
	air	C_6H_{12}	C_6H_{10}	1,3-CHD	1,4-CHD	C_6H_6	air	C_6H_{12}	C_6H_{10}	1,3-CHD	1,4-CHD	C_6H_6
GC 1	43	. .	146	189	. .	388.5	0.228	. .	0.772	1.00	. .	2.06
GC 2	. .	. .	140	193	. .	385	. .	. .	0.726	1.00	. .	2.06
GC 3	43	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .
GC 4	39	. .	130	171.5	260.5	346.5	0.228	. .	0.759	1.00	1.52	2.02
GC 5	27.5	49	79	102	. .	192	0.274	0.48	0.775	1.00	. .	1.88

*chart speed = 40 inches/hour

**$(RT)_r = (RT)_a/(RT)_{1,3\text{-CHD}}$

the peaks in sample 2 (non-purified 1,3-CHD only), the amount of each material present could be calculated quantitatively (Table E3).

TABLE E3

QUANTITATIVE AMOUNTS OF IMPURITIES IN 1,3-CHD

Areas	Components		
Sample Number	Cyclohexene	1,3-CHD	Benzene
1	12,006	72,090	11,494
2	152	81,772	482
mole fraction, sample 1	0.128	0.745	0.127
relative response factors	0.97	1.00	0.94
mole fraction, sample 2	0.002	0.993	0.005

General Observations:

1. No peaks were observed after that for benzene for retention times up to one hour; thus, under these conditions the method was not sensitive to dimers or oxidation products.

2. The amount of benzene observed was always greater than the amount of cyclohexene in all the samples examined. This inequality might indicate that the resulting cyclohexene continues to undergo further Diels-Adler or oxidation reactions.

3. Cyclohexane and 1,4-CHD do not occur as impurities in this system, but the presence of cyclohexene and benzene has been verified.

II. Polymers and Polymerization Techniques

A. Poly-2,5-dimethyl-2,4-hexadiene. 2,5-dimethyl-2,4-hexadiene was polymerized at -70°C in hexane using boron trifluoride gas according to the procedure given in Macromolecular Synthesis (78). The white powder-like product polymer was isolated by vacuum filtration, washed with acetone, and given a final drying by treatment in a vacuum oven at 50°C for 6 hours. Elemental analysis: Observed 86.98% C, 12.74% H, .17% ash at 1000 C°, nil O. Theoretical 87.3% C, 12.7% H. Fisher-Johns melting range: 225-235°C; previously reported melting point (method was not reported) 260-265°C.

B. Polycyclohexadiene. Anionic polymerization of 1,3-CHD. Anionic polymerizations of 1,3-CHD were conducted in bulk, hexane, benzene, toluene and tetrahydrofuran at various temperatures with n-butyllithium as the initiator. A list of these products, the conditions used for polymerization, and some of the properties of the products have been collected into Table A, Appendix 7. Three general experimental techniques were used to synthesize these samples:

1. Vacuum line technique: A high vacuum system was equipped with greaseless, Teflon stopcocks and O-ring type connecting joints. A three-way

distillation manifold (Appendix 2, Figure 2) was used which allowed vacuum bulbs to be backflooded with prepurified nitrogen, removed from the line, and capped with a rubber septum. Stirring was accomplished with Teflon-coated magnetic stir bars, and temperature control was attained through the use of cold baths contained in dewar flasks. For polymerization, a 250 ml vacuum bulb was attached to the manifold and both were extensively flamed while open to vacuum. The distillation manifold was separated from the main vacuum, allowed to cool, and the desired amount of solvent distilled in from a solvent-n-butyllithium solution in an adjacent bulb. The polymerization bulb was then backflooded with nitrogen, removed, and a rubber septum quickly put in place. The desired amount of initiator was injected under the surface of the solvent using a syringe and six inch needle. The bulb was replaced and again evacuated causing a slight loss of solvent. Monomer was distilled in from a third bulb where it had been stirred with initiator (1 ml of 1.6 or 2.25M n-butyllithium solution to about 5 mls of monomer) until color developed.

2. Serum capped cylinder technique. A 75 ml glass cylinder (22 x 150 mm) was fused to one side of a pressure stopcock having a Teflon plug, while a short length of glass tubing just large enough to accommodate a serum cap was fused to the other side (Appendix 2, Figure 2). The apparatus was preheated to approximately 130°C for several hours in an oven. After removal it was purged with nitrogen for about 30 minutes during which it was reheated two or three times with a hand torch. After the final heating it was allowed to cool to room temperature, and the Teflon plug and serum cap inserted. Solvent and monomer were introduced by syringe. The system was pressure equilibrated with nitrogen at the desired polymerization temperature and the initiator added.

3. Anionic polymerization with additives. (a) Addition of tetramethylethylenediamine. Several polymerization reactions in non-polar media were conducted with tetramethylethylenediamine as an additive. The individual conditions for these syntheses are summarized in Appendix 7, Table A. Normally, the desired amount of previously purified liquid diamine was injected using 250 microliter syringe into the vacuum bulb or reaction cylinder

just after the initiator had been added according to the procedures above. (b) Addition of n-butyllithium-carbon dioxide additive. Results of these polymerizations are summarized in Table A, Appendix 7. The additive was generated in situ by first injecting 4 ml of 1.6M n-butyllithium solution into a serum capped reaction cylinder already containing the desired amount of solvent (30-40 ml). Next, 150 cc of Matheson bone dry grade carbon dioxide gas was injected by syringe into the cylinder and the Teflon stopcock closed forcing the reactents to remain in contact. Reaction took place readily with the evolution of heat and formation of a cloudy, gell like precipitate (salts from n-butyllithium and carbon dioxide. After a few minutes of manual shaking, the stopcock was reopened to relieve excess pressure. Following this, the monomer and n-butyllithium initiator were injected in the usual manner by syringe. Further initiator was added until the color change characteristic of carbanion formation occurred. This color change indicated the point at which any residual carbon dioxide or other impurities had been destroyed or neutralized by reaction with n-butyllithium; initiator concentrations quoted refer to amounts added beyond this level.

Ziegler-Natta polymerizations. 1) Using triisobutylaluminum-vanadium trichloride initiator system. A 250 ml three neck flask was heated to 125°C, purged with nitrogen while hot, and stoppered. After cooling the flash was placed in a dry bag under nitrogen, and 0.104 gm (6.6×10^{-4} mole) of vanadium trichloride were weighed in and a Teflon stir bar added. The flash was fitted with nitrogen inlet and outlet adapters and a self-sealing rubber septum cap. 75 ml of purified cyclohexane was injected into the flask by syringe and a slow nitrogen stream allowed to pass through the system. Next, 250 ul of a solution initially containing 8.5 ml of triisobutyl-aluminum in 20 ml of n-hexane, (theoretically containing 5×10^{-4} mole of active triisobutylaluminum) was injected by syringe. The components were allowed to age for 30 minutes with stirring, during which time a finely divided purple solid formed. Lastly, 2.5 ml (0.025 mole) of monomer was added and the system allowed to react for one day with stirring. A small (~1%) yield of product results. Softening point 96-102°C. 2) Using triisobutyl-aluminum-titanium tetrachloride. A Teflon stir bar and 100 ml of purified n-hexane were injected into a flamed and nitrogen purged 250 ml three neck flask. The flask was equipped with gas inlet and outlet adapters and a

self-sealing septum cap. To this, 0.5 ml (0.0045 mole) of titanium tetrachloride and 2.6 ml of 30% v/v triisobutyl-aluminum in n-hexane (0.005 moles active product) were injected into the flask. A dark brown precipitate formed which was allowed to age 30 minutes. 5 ml (0.052 mole) of 1,3-CHD was added by syringe. The reaction was allowed to proceed at room temperature for one day. Yield: 1.2 g, 28%. Elemental analysis: Observed 90.00%C, 10.09%H; Theoretical 89.88%C, 10.12%H. Infrared spectrum IR-22h, Appendix 3.

Alfin polymerization. An Alfin polymerization of 1,3-CHD was conducted according to the procedure outlined for 1,3 butadiene by Sorenson and Campbell (79). The organometallic reagents and solvent referred to were purchased in sealed containers from Organometallics, Incorporated, Manchester, New Hampshire. A Teflon stir bar was placed into a 8 oz soda bottle containing 250 mls of pentane saturated with 1,3-butadiene gas and the bottle sealed with a rubber septum cap. The bottle was placed in a dry bag filled with nitrogen and 5 ml of the blue colored Alfin catalyst suspension and 8.5 ml (7.14 g; 0.09 mole) of 1,3-CHD was added. The blue color slowly disappeared with stirring over a 15 minute period and a small amount of finely suspended, light grey matter was formed. After

four hours, the remaining 15 mls of catalyst suspension was added. Again, the originally opaque, light blue suspension turned grey within 15 minutes. The system was allowed to react for a total of eight hours, by which time a viscous gell formed. The gel was dissolved by stirring 500 mls of benzene into the system. The dissolved polymer was precipitated into 3,000 ml of a three to one by volume methanol-isopropanol solution. A white, strong rubber-like material results which was dried in a vacuum oven at 50°C for eight hours. Crude yield: 4.86 g (68%). The material was purified further by dissolving in purified toluene (3/4% solids by weight), preforming suction filtration to remove suspended matter, and reprecipitating from methanol. Residual solvent was removed by vacuum treatment for 12 hours on the high vacuum manifold. Elemental analysis: Observed 88.62%C, 10.72%H, 0.21%0 and .41% ash; Theoretical 89.88%C, 10.12%H. Infrared spectrum IR-1, Appendix 3.

C. Cis-1,4-polybutadiene. A sample of this polymer provided by the Phillips Petroleum Company had the following structure: 93% cis, 6% trans, 1% vinyl. The number average molecular weight was 100,000. To purify the polymer a 2% solution was made up in benzene, filtered with a sintered glass funnel and reprecipitated from methanol.

The material was dried *in vacuuo* for 24 hours and stored under nitrogen in capped bottles.

D. Trans-1,4-polybutadiene. A sample of this polymer provided by the Phillips Petroleum Company and had the structure: 92% *trans*, 6.6% *cis*, 1.4% vinyl. The number average molecular weight was 42,000. Purification of the sample was achieved in the same manner as *cis*-1,4-polybutadiene.

E. Styrene-butadiene random copolymer. A sample of this copolymer was provided by the General Tire and Rubber Company had a composition of 18% by weight styrene (10 mole%), 82% by weight (90 mole%) butadiene. The structure of the butadiene component was 71.5% *trans*, and 28.5% vinyl. The number average molecular weight was $\overline{Mn}$ = 108,000 and Mw/Mn (via GPC) was 6.2. To effect purification a 2% solution was made up in benzene, filtered, and precipitated from methanol. Residual solvent was removed by treatment for 24 hours *in vacuuo* at 50°C.

F. Styrene-butadiene-styrene block copolymer.

A sample of this copolymer was provided by the Shell Oil Company and had a composition of 30% by weight styrene and 70% by weight butadiene. The structure of the polybutadiene component was 52% *trans*, 40% *cis*, and 8% vinyl. Molecular weight and block distribution were 14,000 styrene-65,000 polybutadiene-14,000 styrene;

$[\eta]$ = 1.10 dl/g (ϕCH_3 at 30°C). Purification as preformed in the same manner as for the styrene-butadiene random copolymer except that toluene was used in place of benzene.

G. Cis-polyisoprene. A sample of this polymer was provided by the B. F. Goodrich Company and had a structure of greater than 99% cis; $\bar{M}n$ = 150,000 and $\bar{M}w$ = 400,000. $[\eta]inh$ was specified to be between 4.0 to 4.5 dl/g. The residual ash content was 0.25 to 0.50%. Purification of the polymer was the same as for polybutadiene.

H. Poly-2,3-dimethyl-1,3-butadiene ("methyl rubber"). The polymer was purchased from K and K Labs (lot 79015x) and no characterization information was provided. The crumb-like material was slightly yellowed in color and had a strong odor of residual monomer; physically entrained particulate matter (dirt) was apparent in the sample. Purification was accomplished by treating 10 g of polymer with 250 ml of boiling cyclohexane in a 500 ml Erlenmeyer flask. The cyclohexane swelled the polymer and allowed unreacted monomer, low molecular weight impurities and the particulate matter to be extracted. This extraction was facilitated by crushing the latter into small (1 mm) pieces while heating in the flask. The polymer was isolated by suction filtration, washed with further cyclohexane and then pressed to dryness. The damp material was added to

300 ml of boiling decahydronapthlene (b.p. 190-195°C) which dissolves the polymer slowly (24 hours). An additional 200 ml of solvent was added (producing a 0.4M solution) and the material filtered twice through a sintered-glass funnel to remove residual suspended material. The polymer was retained as a 0.4M solution in decahydronapthalene by storing in a silicone rubber capped Erlenmeyer flask under nitrogen.

I. Polychloroprene (Neoprene). A partially cross-linked black of solid neoprene was provided by Prof. Otto Vogl, Polymer Science and Engineering, University of Massachusetts. The original polymerization occurred spontaneously at room temperature. Chloroprene polymers prepared by emulsion polymerization contain: 70-95% 1,4 trans, 5-30% 1,2 + 3,4 + cis 1,4, head-tail addition 75%, tail-tail + head-head 10-20% each. To purify the polymer 25 g of solid was swelled by placing the material in 500 ml of chlorobenzene for 24 hours. The swelled material was broken into smaller pieces, and the material was refluxed for one week under nitrogen in chlorobenzene. The resulting solution was filtered, cooled, and precipitated into methanol to form a cloudy suspension. This suspension settled after a three-day period in the refrigerator and the polymer was isolated by

decanting of the solvent. The material was a sticky, dark yellow-brown gum, which was treated for 12 hours *in vacuo* at 40°C to remove residual solvents.

III. Termination Mechanism Studies

A. Introduction. Chain terminating reactions in the anionic polymerization of 1,3-CHD should create either characteristic polymer endgroups or low molecular weight reaction byproducts. The purpose of the work described in this section was to utilize ultraviolet and nmr spectroscopy, and gas chromatographic techniques in an attempt to detect these functional groups or byproducts of polymerization.

B. Ultraviolet analysis of polymers. Ultraviolet spectra were obtained in tetrahydrofuran solution between 225 and 300 mu for a series of seven polycyclohexadienes produced under a variety of synthetic conditions. Instrumental conditions have already been noted. Samples were prepared by reprecipitation three times from Spectrograde tetrahydrofuran and methanol, and dried 12 hours *in vacuo* (1-5 mm) at 50°C. Number average molecular weights were determined by vapor phaseomometry for five of the samples. The results of this ultraviolet spectroscopic analysis are summarized in Table E4.

TABLE E4

POLYCYCLOHEXENE SAMPLES ANALYZED BY UV SPECTROSCOPY

Synthetic Conditions solvent-(°C)	Samples	UV Samples		$\bar{M}n$	$[P_n]/l \times 10^4$
		g/l	(moles-mer units/l) $\times 10^2$		
bulk-(25)	P- 26-2	2.540	3.17	. .	. .
tetrahydrofuran-(25)	P- 50-1	3.050	3.80	3100	9.85
tetrahydrofuran-(25)	P-102-3	1.300	1.62	3005	4.33
tetrahydrofuran-(-78)	P-102-1	1.204	1.51	. .	. .
n-butyllithium-carbon dioxide tetrahydrofuran-(-78)	P-102-8	1.344	1.68	6494	2.07
toluene-(0)	P-111-1	2.67	3.34	5299	5.04
benzene-(0)	P-111-2	4.10	5.13	9308	4.40

C. Nmr investigation. 1.2 ml of 1,3-CHD was introduced into each of two nmr tubes which had previously been cleaned and heated to 125° and then purged with prepure nitrogen. One tube was pressure capped and retained as a blank, while 0.2 ml of 2.25M n-butyllithium-hexane solution was added by 250 ml microliter syringe to the second. The tube was capped and the contents mixed. The reaction mixture had the following initial calculated composition (mole fraction basis): 0.868 1,3-CHD, 0.089 n-hexane, 0.034 n-butyllithium, 0.009 benzene. Aromatic protons were observed at 7.15 ppm, olefinic protons at 5.67 ppm and various aliphatic protons at 0.75-2.1 ppm. The peaks were sufficiently separated to allow integration of the number of benzene protons per 1000 protons of all types in the system. The results are given in Table E5. Analysis of a blank sample before and after the reaction indicated 1.02 mole per cent benzene before the 1.03 mole per cent benzene after reaction. Integration showed 98 olefin protons per 100 aliphatic protons (theoretical: 100/100) in the untreated 1,3-CHD.

TABLE E5

FORMATION OF BENZENE DURING 1,3-CHD POLYMERIZATION WITH n-BUTYLLITHIUM

Time (hr)	No. benzene H's per 1000 other protons	No. olefin H's per 100 aliphatic H's
0.00	6.0	70
0.75	8.6	61
3.00	8.4	55
24.00	21.0	28

D. Nmr spectra of polycyclohexadienes. Previous workers have indicated that polycyclohexadienes synthesized by anionic polymerization contain less than the theoretical number of olefin protons on the basis of their nmr spectra (nmr-1,8, Appendix 4). The 60 MHz nmr spectra of a series of polycyclohexadienes synthesized under various conditions were determined in 10-20% w/v solutions in CS_2 at 37°C using tetramethylsilane as the reference (nmr-1, Appendix 4). The relative number of olefin-to-aliphatic protons were determined from peak area ratios using a planimeter. From this ratio the per cent of the theoretical number of olefin H's actually present was determined (Table E6).

E. Gas chromatography and byproduct formation experiment. The apparatus depicted in Figure 3, Appendix 2, was attached to the vacuum manifold (Figure 1, Appendix 2), evacuated and extensively flamed three times. After cooling to room temperature the apparatus was flooded with nitrogen and 1 ml of 2.25M n-butyllithium in hexane solution was added by syringe to compartment A, and 0.1 ml to each of the six compartments labeled E. The apparatus was reevacuated, and the six constrictions near E were fused shut. Pumping was continued for two to three hours to remove hexane solvent. The apparatus was reflooded with

TABLE E6

Nmr OF POLYCYCLOHEXADIENES; RELATIVE NUMBERS OF OLEFIN VS. ALIPHATIC PROTONS

Sample	Synthetic Conditions solvent-(°C)	Aliphatic/Olefin Proton Ratio	% of Theo. No. Olefin H's*
P-102-1	tetrahydrofuran-(-78)	3.56/1	84
P- 50-1	tetrahydrofuran-(25)	3.60/1	83
P-102-3	tetrahydrofuran-(30)	3.51/1	85.5
P-111-2	benzene-(0)	3.20/1	94
P-111-1	toluene-(0)	3.78/1	79
P-100-9	tetrahydrofuran-(30) n-butyllithium-carbon dioxide additive	4.16/1	72
P-102-6	TMEDA additive	3.23/1	92.5

*Based on the ratio of olefinic to aliphatic protons.

nitrogen, and 8 mls of monomer, from which the benzene and cyclohexene content had just been removed by preparative gas chromatography, were added by syringe at side arm B. The monomer was immediately frozen with liquid nitrogen, the apparatus reevacuated, and the constriction at B fused shut. The monomer solution was allowed to warm to room temperature and stirred until initiation was apparent, then 1 ml of monomer was vacuum distilled into a side arm, which was removed by sealing and burning off at C. This procedure was repeated for each side arm. The portion of side arm containing the monomer and initiator were placed in a Dewar flask containing an ice and water bath. At the desired times, (Table E7) the arms were reversed and the remaining low molecular weight materials were distilled over to the collection side. The U-shaped side arm was then fused shut, separated at the mid-point, and each half was saved for further analysis. The polymeric residues were precipitated from methanol and weighed to determine the amount of insoluble polymer formed as a function of time (Table E7). The composition of the liquid volitals were examined by gas chromatography in the manner previously described and this analysis is presented in the Discussion section I-C.

TABLE E7

AMOUNT OF METHANOL INSOLUBLE POLYMER FORMED AS A FUNCTION OF TIME IN THE REACTION BYPRODUCT FORMATION EXPERIMENT

Sample	Time Reacted (hr)	mg Methanol Insoluable Polymer
1	4	nil
2	8-3/4	nil
3	23-1/2	6.2 mg
4	27	24.9 mg
5	44-1/2	61.5 mg

IV. Stereochemistry of Polycyclohexadienes

A. Introduction. The infrared spectra of polycyclohexadienes, and the nmr spectra of polycyclohexanes which may be derived from these by hydrogenation, were observed to exhibit consistent, characteristic features depending upon the conditions of synthesis. Such behavior suggested an observable connection among reaction conditions, polymer structure and reaction mechanism. To a first approximation the microstructure of these polymers may be simulated by the appropriate dimethylcyclohexenes and dimethylcyclohexanes. Thus, the infrared and nmr spectra of model compounds, whose structures are known, can be used as tools

for interpreting the more complex polymer infrared and nmr spectra. Thus, there were two primary purposes in this series of experiments: to synthesize, separate and identify several model compounds otherwise not available, and then to assemble a collection of the infrared and nmr spectra of a range of appropriate model compounds.

B. Synthesis, separation and identification of model compounds. 1. 3,4-dimethylcyclohexyl acetate. 52.5 g (0.4 mole) of 3,4-dimethylcyclohexanol (molecular weight 128; 94% pure by GC-3, Appendix 5) was added dropwise to 80 ml (0.8 mole) of acetic anhydride in a 250 ml three-neck flask to which 3-5 drops of concentrated sulfuric acid had been added as a catalyst. The solution was refluxed for 12 hours and the contents were initially separated by simple distillation. Distillate coming off at less than 200°C (pot temperature) was discarded. The fraction between 200°C and 225°C was retained giving 66.3 g (95.4% conversion) of 3,4-dimethylcyclohexyl acetate (molecular weight 170, bp 210°C). This product was a clear, colorless liquid having the characteristic ester odor. Gas chromatographic analysis (GC 4, Appendix 5) indicated this product contained 90% of mixed 3,4-dimethylcyclohexyl acetate isomers. Structurally definitive infra red bands: (a) (3,4-dimethylcyclohexanol; IR-3, Appendix 3):

3330 cm^{-1} (H-bonded OH stretch); (b) 3,4-dimethylcyclohexyl acetate (IR-4, Appendix 3): over 3000 cm^{-1}, none; 1745 cm^{-1}, strong (ester C = O); 1250 cm^{-1} (ester asymmetric C - O stretch). 2. 3,4 and 4,5-dimethylcyclohexenes. The apparatus and procedure for ester pyrolysis is described in Appendix 2, Figure 4. The assembly equibrated at approximately 400°C and 46.4 g (0.027 mole) of 3,4-dimethylcyclohexyl acetate was pyrolysed at 380-400°C with a drop rate of 1-2 ml/5 min. The product was washed with 100 mls of 25% aqueous sodium bicarbonate solution until carbon dioxide evolution stopped. The layers were separated and the organic portion was rewashed with 100 mls of distilled water and reisolated and dried over anhydrous magnesium sulfate. This material was distilled under nitrogen and the fraction between 175°C and 210°C (pot temperature), consisting of 94% olefin content (GC-5, Appendix 5), was retained. Yield: 5.05 g (14%) of a clear, volital liquid. Principal infrared bands exhibited by mixed olefin fraction (IR-5, Appendix 3): 3010 cm^{-1} (olefinic C-H stretch); 1650 cm^{-1} (C = C stretch); 1367 cm^{-1}; 1244 cm^{-1} (residual ester C - O); 675-800 cm^{-1} multiple bands (C - H out-of-plane deformations for <u>cis</u> disubstituted olefins). The mixture contained approximately equal amounts of at least two principal olefin

isomers, which were partially separable by preparative gas chromatography (GC-5, Appendix 5; Table E9). Reanalysis after GC fractionation (GC-6, Appendix 5) indicated that fraction 3 (4,5 dimethylcyclohexene) contained about 18.5 mole % fraction 2 (3,4-dimethylcyclohexene) and fraction 2 contained about 9 mole % of fraction 3 as principal impurities, respectively.

Nmr spectra (30-35% v/v in carbon disulfide at 37"C): (a) fraction 3 (3,4 dimethylcyclohexene; NMR-2, Appendix 4) 0.9-1.0 ppm unresolved multiplet (CH_3); 1.2-2.2 ppm unresolved multiplets (- CH and $-CH_2-$); 5.43-5.55 ppm unresolved multiplets (olefin C-H). Relative areas: Aliphatic:olefinic = 73:12 = 6:1. (b) fraction 4 (4,5-dimethylcyclohexene; NMR-3, Appendix 4). 0.85 ppm, doublet (CH_3); symmetrical multiplet centered at 1.51 ppm (-CH); symmetrical multiplet centered at 1.87 ppm ($-CH_2-$); unresolved singlet 5.52 ppm (olefinic C-H). Relative areas: methyl: methine + methylene: olefin = 34/33.5/11 = 3/3/1. Infrared spectra: (a) fraction 3 (3,4-dimethylcyclohexene (IR-6, Appendix 3), 3015 cm^{-1} (olefinic C-H str); 1660 cm^{-1} (C = C stretch); 783 cm^{-1}, 750 cm^{-1}, (C-H out-of-plane deformation for cis disubstituted olefin). (b) fraction 4 (4,5 dimethylcyclohexene, IR-7, Appendix 3) 3015 (olefinic C-H stretch);

TABLE E9

SEPARATION OF 3,4- AND 4,5-DIMETHYLCYCLOHEXENES BY PREPARATIVE GAS CHROMATOGRAPHY

Peak No.	Assignment*	Portion (mm)	% Purity After GC Fractionation
1	unknown--not present after GC purification	34.5	. .
2	unknown--not present after GC purification	50.0	. .
3	3,4-dimethylcyclohexene	57.5	91
4	4,5-dimethylcyclohexene	62.5	82

*Of the two olefin isomers, it was anticipated that 4,5-dimethylcyclohexene, having the least steric hindrance about the double band, should interact more strongly with the column packing material and thus, exhibit the greatest retention time. Therefore peak 4 (62.5 mm) was tentatively assigned to the 4,5 isomer and peak 3 (57.5 mm) assigned to the 3,4 isomer. This assignment was supported by nmr analysis (peak 4, peak 3 NMR - 2 vs. NMR - 3) which indicated peak 4 was related to the more symmetric (4,5 isomer) of the two potential products.

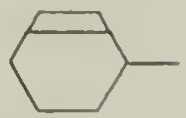
1660 (C = C stretch; cm^{-1}; 758 cm^{-1}, 712 cm^{-1}, (C - H out-of-plane deformation for cis disubstituted olefins).

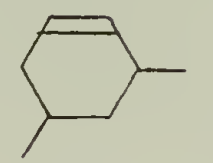
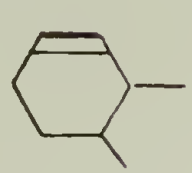
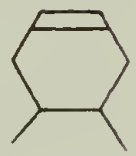
C. Infrared spectra of structurally related low molecular weight compounds. The infrared spectra of a series of low molecular weight compounds, structurally related to polycyclohexene or important in its synthesis, were collected by the procedures indicated in the accompanying table. The spectra determined at our laboratory were run on the neat liquids vs. air reference at medium scan speed. Styrene film (0.05 mm) was used as a wavelength standard based specifically upon the styrene peaks observed at 3027.1, 1601.4, 698.7 cm^{-1} (Table E10).

D. Nmr spectra of model compounds. 1 ml samples of cis-1,2-dimethylcyclohexane and trans-1,2-dimethylcyclohexane of 99.9 (mole) % purity were purchased from the Chemical Samples Company. A series of samples, varying in cis-trans ratio, were made up volumetrically with a 250 ul syringe and 60 MHz nmr spectra were obtained on each as indicated in Table E11. For reference, the known 60 MHz API spectra of these pure compounds, and their related cis and trans 1,4-dimethyl isomers have been included in the table and the nmr spectra collection in Appendix 4, NMR 4-7.

TABLE E10

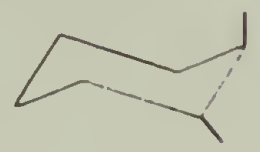
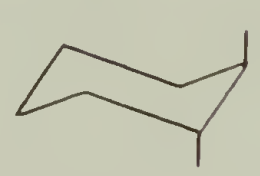
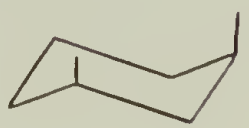
INFRARED SPECTRA OF LOW MOLECULAR WEIGHT MODEL COMPOUNDS

	Compound and Structure	Source	Purity	Spectra	IR Ref. No.
1)	cyclohexane 	this work, purified grade	99%	recorded here	8
2)	cyclohexene 	this work, purified grade	99%	recorded here	9
3)	1,3-CHD 	Columbia Chem. Co.	99%	recorded here	10
4)	2-methylcyclohexene 	CA:68: 82726 g	. .	. .	. .
5)	4-methylcyclohexene 	Phillips	. .	Sadtler No. 7853 .05 mm cell	12
6)	3,6-dimethylcyclohexene 	Chemical Samples Co.	99%	recorded here	2

7)	3,5-dimethylcyclohexene 	Chemical Samples Co.	99%	recorded here	11
8)	3,4-dimethylcyclohexene 	this work	85% + 15% 4,5 isomer	recorded here	6
9)	4,5-dimethylcyclohexene 	this work	90% + 10% 3,4 isomer	recorded here	7
10)	4,4-dimethylcyclohexene 	North-western University (Reference given in Sadtler spectrum No. 12965)	. .	Sadtler No. 12965 .1 mm cell	13

(625-900 cm^{-1} region only for numbers 11a through 11f)

TABLE E10--Continued

	Compound and Structure	Source	Purity	Spectra	IR Ref. No.
11a)	cis-1,2-dimethylcyclohexane 	Socony Oil	99.9	API No. 299 .157 mm cell	14a
11b)	trans-1,2-dimethylcyclohexane 	Socony Oil	99.1	API No. 300 .157 mm cell	14b
11c)	cis-1,3-dimethylcyclohexane 	Socony Oil	98.5	API No. 302 .157 mm cell	14c
11d)	trans-1,3-dimethylcyclohexane 	Socony Oil	97.7	API No. 301 .157 mm cell	14d

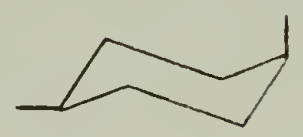
11e)	<u>cis</u>-1,4-dimethylcyclohexane 	Socony Oil	99.0	API No. 303 .157 mm cell	14e
11f)	<u>trans</u>-1,4-dimethylcyclohexane 	Socony Oil	99.6	API No. 304 .157 mm cell	14f

TABLE E11a

Nmr SPECTRA OF A SERIES OF CIS AND TRANS-1,2-DIMETHYLCYCLOHEXANES

Sample	ml cis	ml trans	% cis (vol.)	% trans (vol.)
1	0.250	0.000	100	0
2	0.188	0.062	75	25
3	0.125	0.125	50	50
4	0.083	0.167	33.3	66.7
5	0.050	0.200	20	80
6	0.000	0.250	0	100

conditions: 60 MHz at 37°C

solvent	none
filter bandwidth	4 cps
RF field	0.1 mG
sweep time	500 sec.
sweep width	500 cps.
sweep offset	-0-
spectrum amplitude	1.25

TABLE E11b

Nmr SPECTRA OF PURE 1,2- AND 1,4-DIMETHYLCYCLOHEXANES

Compound	Purity	API No.	NMR Ref.
cis-1,2-dimethylcyclohexane	99.98	453	NMR-4
trans-1,2-dimethylcyclohexane	99.92	554	NMR-5
cis-1,4-dimethylcyclohexane	99.99	455	NMR-6
trans-1,4-dimethylcyclohexane	99.99	556	NMR-7

conditions: 60 MHz at 35°C

solvent	none, run neat
RF field	0.04 mG
sweep time	500 sec.
sweep width	500 cps.
spectrum amplitude	1.0

E. Infrared spectra of polycyclohexadienes synthesized under various reaction conditions. The infrared spectra of a series of polycyclohexadiene samples were obtained on either polymer films cast from 1-2% carbon disulfide solution, or 3-4% sample solutions in carbon disulfide vs. carbon disulfide reference. The cells were 0.2 mm path length; the other instrumental conditions have been noted previously. The 650 cm^{-1} to 800 cm^{-1} region of the spectra, containing the C-H out-of-plane deformations for cis disubstituted olefins, were of principal interest in this set of experiments.

With the exception of the 650 to 800 cm^{-1} regions, the infrared spectra of polycyclohexadienes are largely invariant under a range of reaction conditions. Thus, the intent was to investigate the possible utility of defining microstructural arrangements in terms of characteristic variances observed in this region. The spectra are reproduced in the Discussion, section II-B.

F. Conversion of polycyclohexadienes to polycyclohexane for Nmr evaluation. Introduction and purpose. Polycyclohexane was prepared from polycyclohexadiene by hydrogenation of the precursor with diimide, which is a general reagent for this purpose used extensively for low molecular weight olefins. The procedure described below

TABLE E12

POLYCYCLOHEXADIENE SAMPLES ANALYZED BY INFRARED SPECTROSCOPY

Polymerization Solvent and Sample No.	Temp. (°C)	Film	Sol'n.	Conc. mg/10ml
Tetrahydrofuran				
P- 26- 1	-78	. .	x	418.5
P- 76- 1	-78	x	. .	. .
P-100- 1	-78	x	x	306.3
P-102- 1	-78	. .	x	321.7
P-100- 2	0	. .	x	314.4
P-102- 2	0	. .	x	304.3
P- 50- 1	room temp.	. .	x	620.0
P-102- 3	25	. .	x	317.4
P-100- 3	30	. .	x	314.4
Bulk				
P- 69- 8	room temp.	x	. .	. .
P-119- 2	room temp.	x	. .	. .
Toluene				
P- 69- 1	-78	. .	x	366
P-100- 5	0	. .	x	312.1

TABLE E12--Continued

Polymerization Solvent and Sample No.	Temp. (°C)	Film	Sol'n.	Conc. mg/10ml
P-111- 1	0	x	. .	. .
P-102- 7	25	. .	x	329
P-100- 6	30	. .	x	371
n-Hexane: Tetrahydrofuran: 98:2				
P-128- 1	-78	x	. .	. .
Tetrahydrofuran-n-Butyllithium-Carbon Dioxide				
P-100- 9	-78	. .	x	314.0
P-100-10	-78	. .	x	326.2
P-102- 8	-78	. .	x	327.3
n-Hexane or Cyclohexane-TMEDA				
P-119- 1 (n-hexane)	-78	x	. .	. .
P-100-13 (n-hexane)	-78	x	x	402
P-102- 6	0	. .	x	317.6

TABLE E12--Continued

Polymerization Solvent and Sample No.	Temp. (°C)	Film	Sol'n.	Conc. mg/10ml
Ziegler-Natta in Hexane				
P-104- 6 VCl_3 with $Al(isoBu)_3$	room temp.	x	. .	. .
P-129- 1 $TiCl_4$ with $Al(isoBu)_3$	room temp.	x	. .	. .
Alfin catalyst (pentane)				
P-134- 1	room temp.	x	. .	. .

represents a modification which allows use of the reagent with polymeric substrates. The development of this modification is described in detail elsewhere (see Discussion Section III). Quantitative hydrogenation to polycyclohexane generates a species whose nmr spectrum exhibits characteristic resonances depending upon the

conditions of synthesis of the original polycyclohexadiene. Model compounds suggest these features may be due specifically to the amount of cis vs. trans placement of rings in the polymer chain. The purpose here, then, was to evaluate the possibility of determining the amount of cis-trans ring placement in polycyclohexadienes as a function of synthetic conditions by studying the nmr spectra of polycyclohexanes derived from polycyclohexadiene precursors.

Hydrogenation of polycyclohexadiene with p-toluenesulfonylhydrazide; general procedure. Approximately 1 g of polycyclohexadiene (0.0125 mole) was dissolved in 75 ml of xylene in a 500 ml one-neck flask that previously had been swept with nitrogen. To this solution was added approximately 4.65 g (0.025 mole) of purified p-toluenesulfonylhydrazide which is only slightly soluble at room temperature in aromatic media. A Teflon stirring bar and condenser at its reflux position were put in place and the contents were heated slowly with stirring to reflux (140°C). At 75-80°C the originally two phase system turns turbid and then forms a homogeneous, yellow-orange solution. Reflux was continued for 4-5 hours. During this time a white granular precipitate formed which was removed by vacuum filtration directly after reflux and before

further workup. This material was water soluble and strongly acidic, which are properties characteristic of p-toluenesulfonic acid, the principal anticipated reaction byproduct. The filtrate was allowed to cool in a refrigerator to 5-10°C and the polymer isolated by precipitation from methanol and suction filtration. The product polymer, polycyclohexane, was obtained as a light tan, finely textured powder. This powder was further purified by reprecipitation from cyclohexane and methanol, followed by drying in vacuuo at 50°C for 6-12 hours at 1-5 mm. In this manner the series of polycyclohexanes given in Table C, Appendix 7 were synthesized for eventual nmr analysis.

Characterization. Samples were submitted for elemental (C,H) analysis (Table B,D; Appendix 7) and their infrared spectra (IR-7D, Appendix 3) and Fisher-John's softening points were obtained (Table B,C; Appendix 7). The elemental analysis were used to calculate per cent conversion by the procedures indicated in the appendix. Nmr spectra were run on 7.5 to 20% w/v solutions in carbon disulfide at 37°C, and are described in the Discussion Section II-C.

V. Hydrogenation of Polymeric Substrates with Diimide

A. Introduction and purpose. The diimide hydrogenation technique described above for polychclohexadiene has been extended to a wide range of polymeric substrates. The impirical characteristics and development of this extension are reported here.

B. Hydrogenation of cyclohexene, a model for polycyclohexadiene. 2 mls (1.62 g, 20 mmoles) of cyclohexene and 7.44 g (40 mmoles) of p-toluenesulfonylhydrazide were dissolved in 100 ml of ethylene glycol monomethyl ether and the materials placed in a 250 ml one-neck flask. A Teflon stir bar and a condenser at its reflux position were put in place and the system swept with nitrogen. The contents were reacted at reflux (260°C) for two hours. The solution was cooled to room temperature, and the white solid (sulfinic acid) which formed during the reaction was removed by suction filtration. The product was isolated from the remaining liquid by simple distillation under nitrogen; distillate up to 90°C (pot temperature) was collected and retained for analysis by infrared spectroscopy (IR-15, Appendix 3) and gas chromatography (GC-7, Appendix 5). IR-15 was compared to the known spectra of pure cyclohexene (IR-9) and cyclohexane

(IR-8) indicating the distillate consisted of a mixture of these two materials. Gas chromatographic analysis (GC-7) indicated 77% reduction.

C. Hydrogenation of polycyclohexadiene. In this series of experiments the reaction was conducted in a range or aromatic solvents at reflux which had the effect of changing the reaction temperature. A procedure for the hydrogenation of polycyclohexadiene with p-toluenesulfonylhydrazide in xylene has already been described. With one exception this general procedure remained the same; in the case of mesitylene, the product did not precipitate well from methanol and it was necessary to vacuum distill the solvent to isolate the product. Infrared spectra in carbon disulfide solution and elemental analysis were used to establish the per cent conversion. The calculation procedures and data are compiled in Appendix 7, Tables B-D, and the final results are given below along with a summary of the samples run and the principal reaction parameters (Table E-13). A polycyclohexadiene sample (P-50-1) was characterized before and after its conversion to polycyclohexane (P-54-1) by the procedures indicated below.

1. Elemental analysis

P-50-1	observed	89.47%C	10.33%H	0.2% other	
	calculated	89.88%C	10.12%H	. .	
P-54-1	observed	87.15%C	11.98%H	0.48% O	nil ash
	calculated	87.69%C	12.31%H	nil S	0.39 other

Hydrogen increase per 100 g C + H: 1.74
Theoretical: 2.19

2. Infrared spectra. These were performed in carbon disulfide solution vs. carbon disulfide reference with 0.2 mm cells.

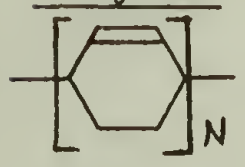
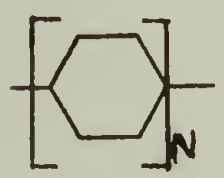
P-50-1	3.13g/l (.039M)	IR-17, Appendix 3
P-54-1	3.07g/l (.038M)	IR-18, Appendix 3

Analytical Bands (P-50-1)	Effect of Hydrogenation (P-54-1)	Assignment
3015 cm^{-1}	completely lost	olefin C-H str.
2920 cm^{-1}	increases	C-H asym. str.
2850 cm^{-1}	increases	C-H sym. str.
1680 cm^{-1}	lost	C=C str.
1650 cm^{-1}	lost	C=C str.
1460 (observed in films only)	increases	CH_2 deformation
765 cm^{-1}	lost	C-H out-of-plane deformation; *cis* olefin
720 cm^{-1}	lost	C-H out-of-plane deformation; *cis* olefin

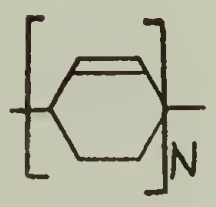
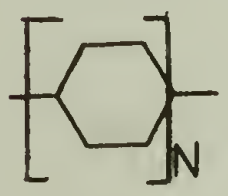
3. Nmr spectra. Determined on carbon disulfide solutions at 37°C and 60 MHz.

Samples	Resonances	Assignment
P-50-1 (NMR-1) Appendix 4	1.5 ppm (partially 2.0 ppm overlapped) 5.64 ppm	aliphatic H aliphatic H olefin H
P-54-1 (NMR -8) Appendix 4	0.75 to 2 ppm (one broad peak) 5.67 ppm 7-8 ppm	various aliphatic protons completely gone none

4. Ultraviolet spectra.

Polymer	Concentration and Solvent
	152.5 mg/50 ml tetrahydrofuran (0.038 M)
	142.4 mg/50 ml (0.035 M)

Adsorbance vs. wave length (mμ).

	=	2100	2200	2300	2400	2500	2600	2700	2800
	. .	2	0.145	0.09	0.09	0.07	0.04	0.03	
	. .	2	1.115*	0.46	0.385	0.32	0.28	0.18	

*Part of a shoulder centered at 225 m

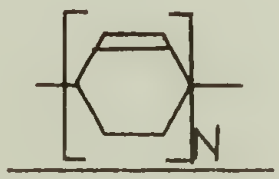
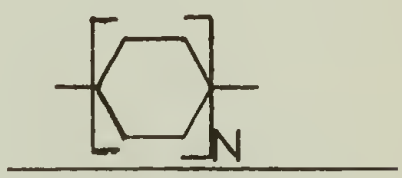
5. Molecular weight before and after hydrogenation.

	P-50-1	P-102-8
before-observed	3160	6500
after-observed	3790[a]	9400[a]
after-calculated	3240[b]	6660[b]

[a]Sample was completely soluble in carbon disulfide and cyclohexane during workup but portions precipitated out in toluene, the solvent available for molecular weight determination. The sample concentrations were redetermined by dry weight after solvent was removed.

[b]Calculated from starting material for no change in degree of polymerization.

6. Solubility behavior of polymer before and after hydrogenation.

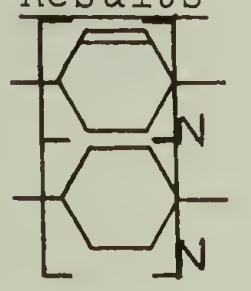
Solvent		
cyclohexane	no	yes
benzene	yes	hot (60°C); with difficulty
toluene	yes	yes, hot
xylene	yes	yes, hot
mesitylene	yes	yes, hot
tetrahydrofuran	yes	no
o-dichlorobenzene	yes	yes
carbon disulfide	yes	yes
alcohols and ketones	no	no

7. Thermal measurements.

DSC scan rate 20°/min; range +40°C to +250°C.

Sample Sizes:	P-50-1	13.1 mg	DSC-1-Appendix 6
	P-54-1	12.8 mg	DSC-1-Appendix 6

Results



Peak DSC (°C)	Softening Range, °C
87.5	101-106
187.0	192-195
Tg = 95	

TABLE E13

PER CENT HYDROGENATION OF POLYCYCLOHEXADIENES
BY p-TOLUENESULFONYLHYDRAZIDE

Sample No.	Solvent	Reflux Temp. (°C)	Volume mls	Moles Polymer
P-39-1	50/50 toluene-ethylene glycol monomethylethu[c]	110	100	P-26-1 10
P-62-1	toluene	110	75	P-50-1 12.6
P-70-1	o-xylene	140	75	P-50-1 13.8
P-79-1	o-xylene	142	75	P-78-1 11.0
P-52-1	mesitylene	160	50	P-26-1,2 6.4
P-54-1	mesitylene	160	125	21.8

[a]May be artifically low due to less than theoretical olefin content in precursor polymer.

[b]Obtained on Fisher-Johns apparatus.

[c]Two phase system.

TABLE E13--Continued

Reactants	Reaction Time (hrs)	% Conversion		Polymer Softening Range (°C)[b]
P-TSH		IR	Elemental Analysis[a]	
20	4	48	40	. .
27	6	78	. .	. .
30.2	5	97	89	197-205
24.1	5	100	. .	230-240
18.7	3	95	98	214-220
43.5	3	95	91	192- 95

D. Hydrogenation with p-toluenesulfonylhydrazide; effect of altering the polymeric substrate. Introduction and summary of results. In this investigation a variety of polymeric substrates were hydrogenated in order to observe the effect of different molecular groupings about the residual double bond of the polymer on the utility of the reaction. The general procedure involved mixing p-toluenesulfonylhydrazide and the polymer substrate in the desired solvent, flushing the system with nitrogen, and then refluxing for the specified time, usually three to six hours. The systems become homogeneous around temperatures of 70-80°C. Table E14 summarizes the substrates and the composition of the reaction systems used. The workups, purification and characterizations for each sample varied somewhat and these are described separately in the next general sections.

Trans-1,4-polybutadiene. The samples were isolated initially by direct precipitation from methanol, after cooling and stirring with 50 mls of a 10% w/v solution of sodium bicarbonate to remove the p-toluene sulfinic acid byproduct. The precipitated polymers were collected by suction filtration and further purified as follows: P-46-1 was dissolved in carbon disulfide (Fisher certified grade) and reprecipitated from methanol twice. P-47-1 was

TABLE E14

POLYMERIC SUBSTRATES REDUCED WITH DIIMIDE

Starting Material	Hydrog. Prod.	Polymer, g
trans-1,4-polybutadiene (PBD-Ht-1)	P- 46-1	1
	P- 47-1	1
	P- 72-2	1
styrene-butadiene-styrene block copolymer (SBS-B-1)	SBS-B-2	2
	SBS-B-3	
Polycyclohexadiene	P- 70-1	1.12
Cis-1,4-polyisoprene (PI-1)	PI-2	1
	PI-3	
Methyl rubber (P-121-1)	P-121-2	75 mls. .4M/DCH
Poly-2,5-dimethyl 2,4-hexadiene (P-123-1)	P-123-2	1.00
	P-123-3	1.00
	P-123-4	1.00
Poly-2-chlorobutadiene (P-126-1)	P-126-2	0.50

[a] pTSH = p-toluenesulfonylhydrazide

[b] DCH = decohydronapthalene

TABLE E14--Continued

Olefin Content Moles	pTSH[a] g	pTSH[a] Moles	Solvent	Vol., ml	Reaction Time, hr.
0.018	6.7	0.036	diphenyl ether	75	3-1/2
0.018	6.7	0.036	mesitylene	75	3-1/2
0.018	6.9	0.037	xylene	75	4-1/2
0.026	9.7	0.052	xylene	150	1/2 4
0.014	5.6	0.030	xylene	75	5
0.015	5.6	0.03	xylene	100	3 4
0.030	11.2	0.06	DCH[b]/ xylene	75 125	12
0.009	3.53	0.018	DCH/ xylene	25 50	4
0.009	3.53	0.018	DCH/ xylene	25 50	4
0.009	3.50	0.018	DCH/ xylene	25 50	4
0.0058	2.20	0.0116	xylene	40	4

dissolved in mesitylene and reprecipitated from methanol. Residual solvent was removed by vacuum treatment for four to six hours at 40°C. This sample (P-47-1) was observed to be insoluble in carbon disulfide. P-72-2 was treated the same as P-47-1 except xylene was used as the solvent; this sample was also insoluble in carbon disulfide.

1. Elemental analysis.

Hydrogenated polybutadienes			
P-46-1	86.14% C	9.38% H	4.48% other
P-72-2	84.13% C	12.99% H	2.88% other
Calculated for polyethylene	85.7 % C	14.3 % H	

(<u>trans</u>-1,4-polybutadiene)

P-72-1	88.03% C	10.96% H	0.38% O	0.5% ash
Calculated for polybutadiene	88.89% C	11.10% H		

2. Infrared spectra were obtained on carbon disulfide solutions or films as follows:

<u>trans</u>-1,4-polybutadiene	2.89 g/l in carbon disulfide vs. carbon disulfide w/0.2 mm cell	IR-31-A
P-46-1	4.0 g/l in carbon disulfide vs. carbon disulfide w/0.2 mm cell	IR-19a
P-47-1	film cast from mesitylene	IR-19b
P-72-2	film cast from xylene	IR-19c

Analytical Bands Trans-1,4-Polybutadiene	Effect of Hydrogenation (P-47-1 and P-72-2)	Assignment
3020 cm^{-1}	lost completely	olefinic C-H stretch
2980 cm^{-1}	lost completely	C-H stretch
2915 cm^{-1}	increases and shifts to 2925	C-H asymmetric stretch
2840 cm^{-1}	increases and shifts to 2850	C-H symmetric stretch
1660 cm^{-1}	lost completely	C = C stretch
1420 cm^{-1}	increases and shifts to 1465 and 1472 cm^{-1}	$C-H_2$ bending
965 cm^{-1} (strong)	lost completely	trans C-H out of plane deformation
910 cm^{-1}	lost completely	same; vinyl contribution
720 and 730 cm^{-1}	new band in products	C-H rock

3. Calculation of per cent of hydrogenation.

Infrared spectra of P-47-1 and P-72-2 films indicated complete loss of bands attributable to olefinic content. On this basis, reduction was close to quantitative. The per cent residual unsaturation for polymer 72-2 may also be calculated from the observed elemental analysis by the relationship %U = 2fc - fh/0.2 (see Appendix 7, Table D for derivation), where fc and fh are the mole per cent of carbon and hydrogen in the hydrogenated sample. For P-72-2 this gives fc = 0.351; fh = 0.649; and %U = 26.5; thus, % conversion = 73.5%.

4. Thermal analysis by DSC at scan rates of 20°/min and 10°/min over the range 30°C to 150°C. Samples: P-72-2, 10.4 mg (DSC-2).

Sample		Tm, °C	Ref.	Softening Point, °C
P-47-1		. .		106-110
P-72-2	20°/min.	121.5	DSC-2	108-111
	10°/min.	118.5	DSC-2	
trans-1,4-polybutadiene		. .		84- 88

Hydrogenation of styrene-butadiene-styrene (SBS) block copolymer with p-toluenesulfonylhydrazide. 2 g of SBS block copolymer (SBS-B-1, 0.026 mole olefin content) was combined with 9.7 g (0.052 mole) of p-toluenesulfonyl-hydrazide in 150 ml of xylene and, with the exception of a small aliquot (SBS-B-2) removed after 30 min, was allowed to reflux for four hours under nitrogen. The solution was cooled, filtered, and the product (SBS-B-3) precipitated from methanol. SBS-B-2 was reprecipitated from purified benzene into methanol and SBS-B-3 from xylene into methanol. Both were dried in vacuuo at 50°C for twelve hours.

Characterization:

1. Elemental analysis*

SBS-B-1	observed	89.04% C	9.66% H	1.32% O nil, ash
	calculated	89.92% C	10.08% H	
SBS-B-2	observed	86.71% C	11.84% H	1.45% other
SBS-B-3	observed	86.44% C	11.97% H	1.60% other
(100% reduction)	calculated	87.64% C	12.36% H	

*assumes 70% by weight butadiene units
30% by weight styrene units

2. Infrared spectra.

Sample	Films Cast From Solvent	Infrared Ref
SBS-1	cyclohexane	20a
styrene (only)	0.05 mm IR ref Film	21
SBS-2	toluene	20b
SBS-3	toluene	20c

Analytical Bands[a] (SBS-1)	Effect of Hydrogenation (SBS-3)	Assignment
1640 cm^{-1}	completely lost	<u>cis</u> C=C stretch
1654 cm^{-1}	completely lost	<u>trans</u> C=C stretch
965 cm^{-1}	completely lost	out of plane deformation (<u>trans</u>)
910 cm^{-1}[b]	considerable reduction	out of plane deformation (vinyl)

Notes:

[a]The bands in the region 3000 cm^{-1} (olefin C-H stretch), 1460-70 cm^{-1}, and 700-800 cm^{-1} (<u>cis</u>

olefin)cm^{-1}, useful in analyzing butadiene homopolymer spectra, are obscured by strong styrene adsorptions in SBS systems (see styrene reference spectra, IR-21).

[b]907 cm^{-1} styrene band (medium intensity) overlaps with (strong) 910 cm^{-1} vinyl band (see styrene reference, IR-32). 720-730 cm^{-1} are new bands which appear between the strong 699 and 750 cm^{-1} styrene bands.

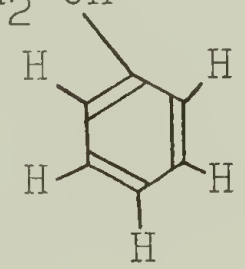
3. Nmr spectra. The nmr spectra of samples were determined in carbon disulfide solution at 37°C.

Sample	Solution Concentration	Ref
SBS-B-1	7.5% w/v	NMR-9
SBS-B-2	7.5% w/v	NMR-10
SBS-B-3	Hydrogenated polymer not soluble at low temperature	

Peak positions and assignments

A D D A
$-CH_2-CH=CH-CH_2-$

B C
$-CH_2-CH-$



E

F
$-CH_2-_n$

Types of protons present in partially hydrogenated SBS copolymers.

Proton	Position (ppm)	SBS-B-1 Observed	SBS-B-1 Calculated*	SBS-B-2 Observed
B,C	1.42	5.2	4.2	7.2
A	2.00	. .	. .	. .
F	1.22	. .	. .	. .
SSB	2.52	. .	. .	. .
D (small)	5.00	2.4	1.8	0.19
D	5.32	. .	. .	. .
E	6.48	1.0	1.0	1.0
E	6.95	. .	. .	. .

*Calculation based on this analysis gives composition 76% PBD 24% Styrene.

4. Thermal analysis. Thermal analysis was obtained by DSC at scan rates of 20°/min and 5°/min; temperature range 35°C to 135°C.

Samples	Weight, mg	Area/mg (Sq Inch) R=4	Area/mg (Sq Inch) R=8	Tm 20°/min. (°C)	Tm 5°/min. (°C)	DSC Ref
SBS-2	7.9 (5.5 PBD)	0.367	0.169	66	70.3	3a
SBS-3	9.8 (6.9 PBD)	0.698	0.324	97	91.8	3b

5. Calculation of per cent hydrogenation. The percentage of hydrogenation was determined by elemental and nmr analysis.

Elemental analysis: The weight of hydrogen uptake observed divided by the amount which would be taken up theoretically in a 100% hydrogenation (2.28% theoretically for 70-30 copolymer) gives the per cent hydrogenation by elemental analysis.

Sample	% H	% H corr. to 100% C and H	H increase	% Conv.
SBS-B-1	9.66	9.78	. .	. .
SBS-B-2	11.84	12.01	2.23	97
SBS-B-3	11.97	12.16	2.38	104

nmr (SBS-B-2): The relative number of vinyl protons to ring protons goes from 2.4/1.0 (SBS-B-1) to 0.19/1.0 (SBS-B-2). Taking into account a statistical factor of 2.5, the number of butadiene units (intact) per each ring (styrene) unit is calculated as 6.00 in SBS-B-1, which decreases to 0.47 in SBS-B-2. This corresponds to a 92% hydrogenation.

Infrared: Because film spectra were obtained, it was not possible to use a Beer's law calculation, however, the infrared for SBS-B-2 showed residual olefin content at 965 and 1650 cm^{-1} while that for SBS-3 shows complete loss of peaks attributable to olefin structure ($\sim$100% conversion).

Cis-1,4-polyisoprene. One sample (PI-2) was removed after three hours of reflux for infrared analysis. The remainder (PI-3 reacted a total of 4 hr) was cooled, filtered, and precipitated from xylene into methanol. The hydrogenated product (a strong rubber) was further purified by reprecipitation from a benzene solution into

methanol and dried by vacuum treatment at 50°C for twenty-four hours.

Characterization:

1. Elemental analysis.

PI-1	observed	87.63% C	11.57% H	0.8 % other
	calculated	88.17% C	11.84% H	. .
PI-3 (100% Hydrogenated)	observed	85.30% C	13.75% H	0.95% other
	calculated	85.80% C	14.20% H	. .

2. Infrared spectra.

Sample	Films Cast From Solvent	IR Ref
PI-1	benzene	22
PI-2	xylene	23
PI-3	xylene	23

Analytical Bands, cm^{-1} (PI-1)	Effect of Hydrogenation (PI-2 and 3)	Assignment
3050	completely lost	olefinic C-H stretch
1680	completely lost	C=C stretch
835	completely lost	C-H out of plane deformation

3. Nmr spectra (Appendix 4). Nmr spectra were determined on samples dissolved in carbon disulfide and deutero chloroform at 37°C.

Sample	Solution Concentration	Solvent	
PI-1	7.5% w/v	carbon disulfide	NMR-11
PI-3	7.5% w/v	deutero chloroform	NMR-12

Peak positions, assignments, relative areas.

Sample	Position (ppm)	Assignment	Relative Area Observed	Relative Area Calculated
PI-1	1.64 (singlet)	CH_3	2.95	3.00
	1.95, 2.00 (doublet)	CH_2	4.20	
	5.04 (unresolved multiplet)	vinyl	1.00	1.00
PI-3	0.77, 0.98 (doublet	CH_3	1.00	1.00
	1.23 multiplet center, broad peak 1.0 to 2.1 ppm			

The peak at 5.04 ppm was completely gone, while the peak at 7.3 ppm was found to be caused by contamination of the nmr solvent by benzene.

4. Thermal analysis. Thermal analysis was preformed with the DSC at a scan rate of 20°/min over a temperature range -80°C to +300°C, sample size 13.2 mg. For PI-3, one transition (Tg) was observed at -61°C (see DSC-4, Appendix 6).

5. Number average molecular weight. The number average molecular weight after hydrogenation of PI-3 was $\overline{M}n$ = 122,800 as determined by membrane osmometry at 37°C in $CHCl_3$.

6. Calculation of per cent reduction. Nmr and infrared spectra both indicated no residual olefin content in PI-2 and 3. The amount of hydrogen uptake observed by elemental analysis (PI-1 vs. PI-3) divided by the amount which would be taken up theoretically in a 100% hydrogenation indicated a conversion of 94% had been achieved.

Poly-2,3-dimethylbutadiene. The reaction mixture was cooled and filtered to remove insoluble matter. Direct precipitation from methanol was attempted but this method yielded a very fine, nonfilterable material. Thus, decahydronapthalene and xylene were removed by distillation on the vacuum manifold to give a very viscous, yellow orange liquid. The product was methanol insoluble but could be further fractionated with hexane. One fraction was a hexane insoluble, white powder (a byproduct), the main portion, and desired product, was a hexane soluble, viscous liquid (P-121-2).

Characterization:

1. Elemental analysis.

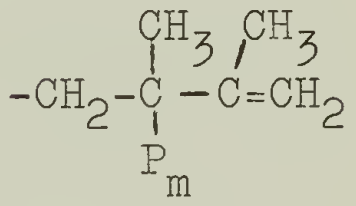
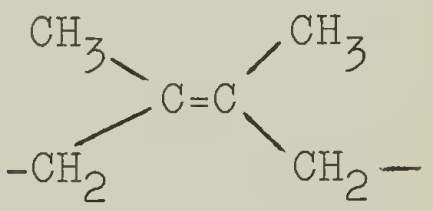
P-121-1	observed	82.84% C	10.63% H	4.41% O	1.2% ash*
	calculated	87.80% C	12.20% H		

*after C_6H_{12} extraction; before extraction with cyclohexane, 3.4% ash.

P-121-2	observed	83.36% C	12.02% H	4.47% O	ash, nil
	calculated	85.70% C	14.30% H	. .	. .
hexane insoluble byproduct	observed	60.49% C	5.15% H	34.36% other	

2. Infrared spectra.

Sample	Films Cast From Solvent	IR Ref
P-121-2	decahydronapthalene	24
P-121-2	hexane	25

Analytical Bands, cm^{-1} (P-121-1)	Effect of Hydrogenation (P-121-2)	Assignment
$1645 cm^{-1}$	decreases considerably	C=C str. in 
$1690 cm^{-1}$	decreases considerably	C=C str. in 
$1730 cm^{-1}$	decreases considerably	

3. Nmr spectra. The nmr spectrum of P-121-2 (product) was obtained from a 10% w/v solution in carbon disulfide at 37°C (NMR-13, Appendix 4).

Peak positions, assignments and relative areas

Position	Assignment*	Relative Area
Hydrogenated Portions		
0.76 ppm	CH_3-C(H)(H)-C-	14.8 total
1.20 ppm	-CH_2-C-	
Unsaturated Portions		
1.60 ppm	CH_3-C=C-	14.0 total
1.94 ppm	-CH_2-C=C-	

*See p 216-218

4. Calculation of per cent hydrogenation. The percentage of hydrogenation was determined by elemental and nmr analysis.

Elemental Analysis. The amount of hydrogen uptake (P-121-1 vs. P-121-2) divided by the amount which would be taken up theoretically at 100% hydrogenation gives a calculated conversion of 62.5%.

Nmr analysis. The aliphatic CH_3 and CH_2 protons adjacent to a residual olefin linkage (i.e., those in a non-reduced repeating unit) resonate at 1.60 and 1.94 ppm while hydrogenation of the olefin causes these resonances to shift to 0.76 and 1.20 ppm respectively. There are ten such protons before hydrogenation and twelve after. Taking this statistical factor into account, the areas observed in the P-126-2 nmr (NMR-13) yield the following calculation:

$$\frac{(14.8/6)}{(14.0/5) \text{ and } (14.8/6)} \times 100\% \text{ reduction} = 47\% \text{ reduction.}$$

Both of these analyses are in general agreement with the infrared spectra of P-126-2 which shows considerable, though not complete, loss of C=C stretching bands.

Hydrogenation of poly-2,5-dimethyl-2,4-hexadiene. The reaction mixture was cooled, filtered twice, and placed in the refrigerator under nitrogen. A precipitate formed which was isolated by suction filtration (P-123-2), washed with methanol and dried in vacuuo at 50°C for twelve hours. The remaining reaction solution was vacuum distilled on the high vacuum manifold to yield a second solid residue (P-123-3). A portion of P-123-2 was rehydrogenated under similar conditions to the above in an attempt to force hydrogenation further. This second product was designated P-123-4.

Characterization:

1. Elemental analysis.

P-123-1	observed	86.98%C	12.74%H	0.17% ash	nil O
	calculated	87.30%C	12.70%H	. .	. .
P-123-2	observed	85.98%C	13.00%H	0.21% ash	0.81% O
P-123-3	observed	84.66%C	13.00%H	1.00% ash	1.35% O
P-123-4	observed	85.48%C	12.90%H	0.88% O	0.74% ash
(100% hydrogenated)	calculated	85.7 %C	14.30%H	. .	. .

2. Infrared spectra. Infrared spectra were determined from films melt casted onto salt plates.

Sample	IR Ref.
P-123-1	26
P-123-2	27
P-123-4	27

Analytical Bands, cm^{-1} (P-123-1)	Effect of Hydrogenation (P-123-2,4)	Assignment
3032 cm^{-1}	small decrease	olefin C-H stretch
1675 cm^{-1}	moderate decrease	C=C stretch
1615 (very small) cm^{-1}	not observable	C=C stretch (?)
945 cm^{-1}	slight decrease	C-H out of plane deformation (?)
815 cm^{-1}	slight decrease	C-H out of plane deformation

3. Thermal analysis.

Sample	Softening Points, °C
P-123-1	230-40
P-123-2	215
P-123-4	195

4. Calculation of per cent hydrogenation. Comparison of the amount of hydrogen uptake (0.36% when corrected to 100% C + H) to the theoretical amount for 100% conversion (1.6%) (P-123-1 vs. P-123-2) yields a calculated conversion of 22.5.

Poly-2-chlorobutadiene (neoprene). The product, P-126-2, was isolated by removal of the solvent on a high vacuum manifold. Residual solid was reprecipitated twice in methanol from benzene solutions and dried *in vacuuo* at 50°C for six hours.

Characterization:

1. Elemental analysis.

P-126-1	observed	56.36%C	6.42%H	30.97%Cl	6.25% other
	calculated	54.25%C	5.65%H	40.10%Cl	
P-126-2	observed	55.16%C	6.36%H	28.22%Cl	4.55% O 5.61% ash
	calculated	53.0 %C	7.70%H	39.3 %Cl	

The above analysis corrected to 100% C+H+Cl gives:

P-126-1	60.0 %C	6.85%H	33.15%Cl
P-126-2	61.52%C	7.08%H	31.40%Cl

2. Infrared analysis.

Sample	Film Cast From Solvent	IR Ref.
P-126-1	carbon disulfide	28
P-126-2	benzene	29

Analytical Bands, cm^{-1}	Effect of Hydrogenation	Assignment
3030	all bands remain	olefin C-H stretch
1668	essentially	C=C stretch
800	intact	out of plane C-H deformation
new bands in IR-29	1922 cm^{-1}	unknown
	1600 cm^{-1}	unknown
	1495 cm^{-1}	unknown
	1325 cm^{-1}	unknown
	700 cm^{-1}	CH_2 sequences or olefin C-H out-of-plane deformation

3. Nmr spectra. Nmr spectra were determined on 5-10% carbon disulfide solutions at 37°C.

P-126-1; NMR-14

Position	Assignment	Area
2.2 (singlet)		
2.35 (doublet)	$-CH_2-$	4.10
2.50 (singlet)	next to olefin	
5.41 (multiplet)	olefin H's	1.00

P-126-2; NMR-15

2.2/2.35	$-CH_2-$	not
2.50	as above	determined
5.35	olefin H's	
1.6		
1.2	long sequences, position quite similar to hydrogenated PBD also consistent with peak at 700 cm^{-1} in IR spectrum	

4. Calculation of per cent hydrogenation. Calculation of per cent conversion by hydrogen uptake vs. theoretical hydrogen uptake at 100% conversion indicated 11% hydrogenation.

E. Reduction with p-toluenesulfonylhydrazide; effect of varying the hydrazide-to-olefin ratio in polybutadiene hydrogenation.* The effect of varying the mole ratio of

*Study performed by Mr. William Levinger, Amherst Regional High School, under the author's supervision.

reactents from 0.8 to 2.0 (p-toluenesulfonylhydrazide/olefin) was evaluated in the series of reactions summarized in Table E15. All the reactions were carried out in xylene at a constant reaction time of four hours on cis-1,4-polybutadiene. After reaction, the mixture was cooled and the product isolated by precipitation from methanol. Since crosslinking was a characteristic feature of the study, the materials were purified twice by stirring with purified methanol (0.5 gm polymer/250 ml methanol) and drying in vacuuo for twelve hours at 50°C.

1. Elemental analysis.

No. 4	observed	80.91% C	13.43% H
No. 5	observed	83.77% C	13.54% H
Polyethylene	calculated	85.7 % C	14.3 % H

2. Infrared analysis. Infrared spectra of samples No. 4 and No. 5 were obtained on films cast from xylene. The spectra of the products possessed the characteristic polyethylene bands at 2924, 2850 (C-H stretch), 1473, 1463 (C-H bend) and 730, 720 (CH rock) cm^{-1} and exhibited complete absence of olefinic bands.

F. Hydrogenation with p-toluenesulfonylhydrazide; relative hydrogenation rates of cis and trans polybutadiene.

TABLE E15

EFFECT OF REACTANT RATIO IN THE HYDROGENATION OF CIS-1,4-POLYBUTADIENE

Sample	Cis-1,4-Polybutadiene		pTSH		R = pTSH / olefin	Per Cent	
	Wt., g	Moles	Wt., g	Moles		Insoluble Polymer, %	Soluble, % in Xylene
1	1.03	0.0191	2.99	0.0159	0.83	100	0
2	1.05	0.0194	3.70	0.0196	1.01	100	0
3	1.02	0.0190	4.69	0.0249	1.32	99	trace
4	1.02	0.0190	5.61	0.0298	1.57	4	96
5	1.02	0.0190	7.48	0.0398	2.09	0	100

Cis-1,4-Polybutadiene:

10.21 g (0.055 mole) of p-toluenesulfonylhydrazide was added at the onset of reflux to a solution of 2.00 g (0.037 mole) of cis-1,4-polybutadiene in 100 ml of purified toluene, the system swept with nitrogen and reacted for four hours. The ratio of reactants was 1.48/1.00 p-toluenesulfonylhydrazide/olefin. 5-6 ml aliquots, containing about 100 mg of polymer, were removed at times varying from fifteen minutes to four hours. The samples were isolated by precipitation from methanol, washed twice in fresh methanol and dried at 50°C *in vacuuo* for twelve hours.

Trans-1,4-Polybutadiene:

10.45 g (0.056 mole) of p-toluenesulfonylhydrazide was added to a solution of 2.02 g (0.038 mole) of trans-1,4-polybutadiene in 100 ml of toluene at the onset of reflux. The system was swept with nitrogen and reacted six hours. The ratio of the reactants was 1.50/1.00 p-toluenesulfonyl-hydrazide/olefin. 5-6 mls aliquots were removed at intervals from one-half hour to six hours of reaction time. The samples were isolated by precipitation from methanol, and reprecipitated after a filtration step from xylene solutions into methanol. The samples were dried *in vacuuo* at 60°C for twenty-four hours.

Characterization:

1. Elemental analysis. Elemental analyses were used to calculate per cent conversion vs. time for partially reduced hydrogenated polybutadienes; the procedure and calculations are given in Appendix 7, Tables E1 and E2, and the final results summarized in Table E16 below.

2. Infrared spectra. The infrared spectra of all the samples below were obtained in order to follow the gradual adsorbance band changes which occurred in going from polybutadiene to polyethylene. The significant portions of the spectra are reproduced in Appendix 3, IR-30-A to 30-H (high cis-1,4 series) and IR-31-A to 31-H (high trans-1,4 series).

3. DSC analysis. These analyses are reported in a separate experimental section (cf. Section 7). In general, the DSC analyses were performed to study details of hydrogenation in terms of the increasingly crystallizable structures which occur as hydrogenation proceeds.

G. Hydrogenation with p-toluenesulfonylhydrazide; relative rate of trans vs. vinyl hydrogenation in styrene-butadiene random copolymer (SBS-R). 3.0 g of SBS random copolymer (0.046 mole polybutadiene content) was dissolved in 150 ml of purified toluene. At the onset of reflux, 17.16 g (0.092 mole) of p-toluenesulfonylhydrazide was

TABLE E16

PER CENT HYDROGENATION VS. TIME OF CIS- AND TRANS-1,4-POLYBUTADIENE

Sample	Time (Hrs.)	Per Cent Reduction By Elemental Analysis	IR of Films Cast From Solvent	IR Ref.
		High Cis-1,4 Series		
cis-1	0.00	0	carbon disulfide	30-A
cis-2	0.25	18	carbon disulfide	30-B
cis-3	0.5	33	carbon disulfide	30-C
cis-4	0.75	48	toluene	30-D
cis-5	1.0	55.5	toluene	30-E
cis-6	1.5	76.5	xylene	30-F
cis-7	2.0	78	xylene	30-G
cis-8	4.0	81	xylene	30-H
		High Trans-1,4 Series		
trans-1	0	0	carbon disulfide	31-A
trans-2	0.5	27	carbon disulfide	31-B
trans-3	1	49.5	carbon disulfide	31-C
trans-4	1.5	64.5	carbon disulfide	31-D
trans-5	2	70.5	toluene	31-E
trans-6	3	82.5	toluene	31-F
trans-7	4	79.5	toluene	31-G
trans-8	6	83.0	xylene	31-H

added which dissolved immediately to form a homogeneous solution. Aliquots of 10.15 ml (200-300 mg polymer) were removed at time intervals from ten minutes to one and one-half hours. All samples were precipitated from 250 ml methanol and extracted once with 250 ml of methanol. The samples were dried in vacuuo at room temperature and reprecipitated once more from benzene into methanol, with a filtration step just before the precipitation. These samples were dried twelve hours at 50°C in vacuuo.

Characterization:

1. Elemental analysis. Samples were submitted for elemental analysis and the data used to calculate the per cent conversion as a function of time by comparing the observed hydrogen uptake to that theoretically expected for 100% conversion. The procedure and calculations are given in Appendix 7, Table F1, and the results summarized in Table E17.

2. Infrared spectra. The infrared spectra (IR-32-A to 32-H; Appendix 3) of the products were obtained on films cast from benzene. Because the styrene repeating units were not effected by hydrogenation, these could be used as an internal standard to determine effective film thickness among samples. For this purpose, the styrene

TABLE E17

RELATIVE RATES OF HYDROGENATION OF THE TRANS AND VINYL CONTENT IN STYRENE-BUTADIENE COPOLYMERS

Sample No.	Hydrogenation Time, Min.	Per Cent Conversion		Per Cent Conversion by Infrared		
		Elemental[a]	NMR	Overall Per Cent Hydrogenation	Composition of Residual Unsaturation	
					% trans	% vinyl
SBS-R-0	0	0.00	-7.3	0	29.5[b]	70.5[b]
SBS-R-1	10	17.35	2	5	29.5	70.5
SBS-R-2	20	17.00	12	17.8	31.4	68.6
SBS-R-3	30	36.60	29	23.2	28.3	71.7
SBS-R-4	45	48.30	39	43.6	27.6	72.4
SBS-R-5	60	74.0	46	79.5	17.6	82.4
SBS-R-6	90	74.7	74	84.1	8.9	91.1
SBS-R-7	135	93.5	not sol.	98.0	0	100

[a]Calculations based on 82% polybutadiene (90 mole %) and 18% styrene (10 mole %), which is the composition quoted by supplier.

[b]These values compare to 71.5% trans and 28.5% vinyl, the values provided by supplier.

repeating unit band at 1601.4 cm^{-1} was sufficiently isolated from polybutadiene adsorptions (Appendix 3; IR-32-H of SBS-R-0 vs. IR-21 of styrene film). The relative amounts of trans and vinyl content could be calculated from the observed adsorbances and known extinction coefficients at 965 cm^{-1} and 906 cm^{-1}, respectively, after subtracting a correction for the strong styrene adsorption at 906.7 cm^{-1}, which interfers with the vinyl band of polybutadiene. The overall hydrogenation was calculated by following the decreases in adsorbance at 1650 cm^{-1} (C=C stretching) normalized with respect to film thickness. These results are also summarized in Table E17, and the procedures and calculations are found in Appendix 7, Table F3.

3. Nmr spectra. The nmr spectra of carbon disulfide (SBS-R-1,2,3) and benzene (SBS-R-4,5,6) solutions (10% w/v) of the products were recorded at 37°C and 60 MHz. The ratio of vinyl protons to aliphatic protons of all types (see assignments) was determined by integration, and this ratio was used to calculate per cent conversion as a function of time by nmr. The results are given below and the data and calculations are listed in Appendix 7, Table F2.

Peak Position (ppm) (SBS-R-0)	Assignment	Effect of Hydrogenation (SBS-R-3)
1.95	CH_2 next to ring	shifts
4.96	Terminal vinyl $=CH_2$ (1,2)	becomes smaller
5.30	Internal vinyl (1,4) -C=C-	becomes smaller
7.08	Ring protons	remains constant
. .	. .	. .
1.2	long $-CH_2-$ sequences	new peak in product; increases with per cent reduction

H. Thermal analysis of partially hydrogenated polybutadiene homopolymers and copolymers. The thermal properties of several series of partially hydrogenated butadiene homopolymers and copolymers were studied using the DSC. The range of samples is indicated in Table E18. Thermograms were obtained at two scan rates of 5°C/min. and 29°C/min.; one sample (hydrogenated cis-1,4-polybutadiene) was run at 2.5, 5, 10 and 20°C/min. to determine the effect of scan speed on the observed transition points for these types of polymers.

Normally, each sample was first scanned twice to 10°C above the observed transition and allowed to cool slowly

back to the starting temperature. A third scan was made and the resulting curve recorded. For starting temperatures of 308°K (35°C) and higher, no collant was necessary; starting temperatures lower than this (down to 278°K; +5°C) required an ice/water coolant bath.

From each curve, the temperature corresponding to the maximum point in the curve (i.e., the curve peak) (temperature at which the maximum rate of melting occurs for a given scan rate), the apparent melting point (defined by the point of intersection of a double extrapolation of the curve peak and tail), and the area under the peak were obtained. The latter (in square inches) was measured by using a compensating polar planimeter (Keuffel and Esser No. 62-0015) and normalizing with respect to the mg. of sample involved. All area measurements were performed on curves run at the same scan rate and attentuations.

The DSC measurements and results are summarized in Table E18; redrawn curves have been placed in Appendix 6, DSC-2 to DSC-6.

TABLE E18

THERMAL PROPERTIES OF PARTIALLY HYDROGENATED BUTADIENE HOMOPOLYMERS AND COPOLYMERS

Sample	Range Meas. (K°)	Peak Max. (T°C) 20°C/min Scan Rate	Apparent Melting Point	
			5°C/min	20°C/min
				High Trans-
PBD-Ht-8	303-450	104	102.25	106.0
PBD-Ht-7	303-453	96	96.0	98.0
PBD-Ht-6	298-458	87	87.5	89.0
PBD-Ht-5	293-458	74	77.4	80.5
PBD-Ht-4	298-463	62	64.75	68.0
PBD-Ht-3, 2,1[b]	293-458	. .	. .	. .
				High Cis-
PBD-Hc-8	308-423	92	96.1	98.0
PBD-Hc-7	308-423	69	78.0	78.0
PBD-Hc-6	293-408	59	62.5	65.0
PBD-Hc-5	283-450	37	41.8	43.5
PBD-Hc-4, 3,2,1[b]	283-458	. .	. .	. .

[a]Includes a correction of -2°C based upon the observed melting points of benzoic acid and adipic acid used as standards.

[b]No observed transitions.

[c]Figure in parenthesis indicates the weight of the butadiene component in the copolymer.

[d]Hydrogenated four hours in refluxing xylene at a reactant ratio of $\frac{PTSH}{(PBD)} = 2/1$.

TABLE E18--Continued

Sample Areas (sq. in.; Avg. 3 Determinations)	Mg Sample	Area/ Mg	DSC Ref. No. Appendix 6
1,4 Series			
6.65	11.3	0.588	5
4.51	10.2	0.448	5
4.58	11.9	0.385	5
2.00	6.2	0.322	5
3.60	12.6	0.287	5
. .	. .	. .	. .
1,4 Series			
3.09	9.8	0.315	6
2.26	11.0	0.206	6
2.29	12.2	0.188	6
2.63	20.7	0.127	6
. .	. .	. .	. .

TABLE E18--Continued

Sample	Range Meas. (K°)	Peak Max. (T°C) - 20°C/min Scan Rate	Apparent Melting Point	
			5°C/min	20°C/min
			Styrene-butadiene-styrene	
SBS-3	313-403	91	91.75	94.0
SBS-2	308-528	67	70.25	72.0
SBS-1	326-593	none	. .	. .
			DSC Behavior of Completely	
cis-poly-butadiene	273-423	100	106.5	113.5
		Peak Maximum Temperatures (uncorrected)		
				T(obs), °C
				115.5 109.5 106.5 105.75
trans-poly-butadiene	313-423	117.5	118.0 (10°/min.)	121.5
		113.5 (10°/min.)		

TABLE E18--Continued

Sample Areas (sq. in.; Avg. 3 Determinations)	Mg Sample	Area/ Mg	DSC Ref. No. Appendix 6
Copolymer Series			
4.78	9.8 (6.85)[c]	0.697	3
2.02	7.9 (5.5)	0.367	3
. .	16.2 (11.3)	. .	3
Hydrogenated Polybutadiene Samples[d]			
7.29	15.1	0.483	2
as a Function of Scan Rate			
Rate, °C/min			
20.0			
10.0			
5.0			
2.5			
6.48	10.2	0.622	2

DISCUSSION

I. Molecular Weight Limiting Reactions in the Anionic Polymerization of 1,3-Cyclohexadiene

A. Introduction and general features. 1,3-CHD has been polymerized by numerous techniques (p 19) and, of these, anionic polymerization is the most advantageous in regard to molecular weight and conversion. However, even with the anionic method there are no reported instances of molecular weights above 20,000. It seems molecular weight limitation is intrinsic to the monomer, and it was desired to develop an understanding of this problem in relation to the present studies on this polymerization system. The following discussion will hope to show that molecular weight is limited by chain transfer to monomer, a condition evidenced by both the formation of low molecular weight reaction byproducts and the structure of the polymer chain end.

B. Comments on previously postulated termination mechanisms. Previous workers (pp 30-34) have postulated on molecular weight limitation in the anionic polymerization of 1,3-CHD. The hydride elimination and solvent reaction schemes (Figure R9) reviewed previously are correct in principle but are known to be kinetically quite slow relative to polymerization and are associated with

aging of "living polymer" solutions (82); hence, it is doubtful that these play an important role in molecular weight limitation. The allylic abstraction scheme of Lussi and Barman (Figure R11), involving abstraction of an allylic proton from a monomer by the growing polymer to terminate the chain, is more plausible considering the reactivity of such protons. Furthermore, there are independent studies which lend further weight to this postulation. Bates, Carnigham, and Staples (p 8) have shown that both 1,3-CHD and 1,4-CHD are susceptible to allylic abstraction by strong organic bases (potassium tert.-amyl oxide) and that abstraction occurs via a common anion. Here, it was useful to view such strong organic bases as low molecular weight analogs of the polymeric carbanion involved in anionic polymerization.

More direct support was presented in the unpublished study (p 12) of Lenz and Adrian who demonstrated that 1,4-CHD is aromatized in polar media by contact with n-butyllithium, the specific initiator used in anionic polymerization. Presumably, abstraction of allylic protons and a cyclohexadienyl carbanion intermediate were involved. Further, Yamaguchi et al. (20) have shown that 1,4-CHD is a highly effective chain transfer agent in anionic polymerization (Li counterion) of 1,3-CHD. Taken together,

these studies indicate that 1,4-CHD is susceptible to allylic abstraction under the specific conditions of anionic polymerization, and along with its related 1,3-isomer, is susceptible to attack by strong organic bases.

The Lussi-Barman scheme, if correct, has some important characteristic features which are potentially observable. Detection of these features would verify the mechanism and serve to differentiate among several suggested alternatives which could occur after the initial allylic abstraction (Figure R11). If the cyclohexadienyl carbanion resulting from allylic abstraction immediately reinitiates polymerization the resulting chain will be characterized by a terminal cyclohexadiene unit. This allows for molecular weight, but not conversion, limitation. Alternately, this species may eliminate lithium hydride to form benzene which would occur as a low molecular weight reaction byproduct. If the lithium hydride thus eliminated is inert, this mechanism requires limitation in molecular weight and conversion. In this regard, Lussi and Barman suggested a reinitiation step involving lithium hydride; however, there is no known evidence that lithium hydride alone initiates the anionic polymerization of even the most active monomers (81). The inertness of lithium hydride contrasts the behavior of

lithium alummum hydride which is an initiator for polymerization (81); the difference might be accounted for on the basis of lithium hydride insolubility in most polymerization media.

C. Current studies on chain transfer reactions during the anionic polymerization of 1,3-CHD. 1,3-CHD was treated with n-butyllithium as a "base" and changes in the benzene content were observed by nmr spectroscopy (p 98). The results summarized on Table E5 (p 98) and in Figure D1 indicate an increase in benzene as judged by an increase in aromatic proton resonances from 0.6 to 2.1% over a period of 24 hours. Apparently, as in the case of 1,4-CHD, benzene is formed by abstraction of allylic protons from 1,3-CHD followed by aromatization (Figure D2).

FIGURE D2. Abstraction of Allylic Protons from 1,3-CHD.

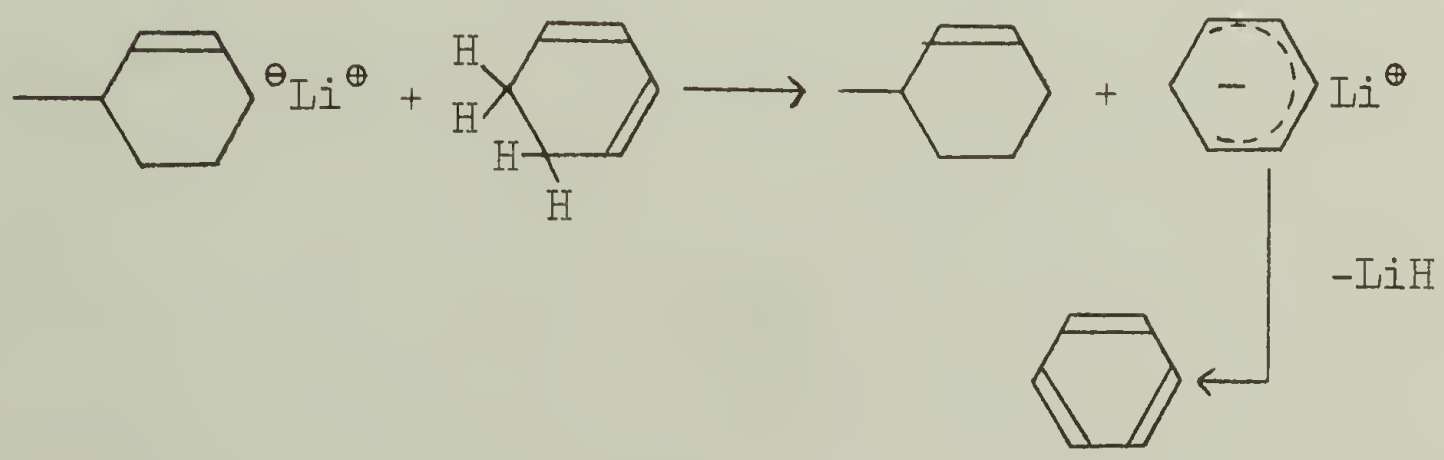


Figure D 1. Aromatization of 1,3-Cyclohexadienes during Anionic Polymerization.

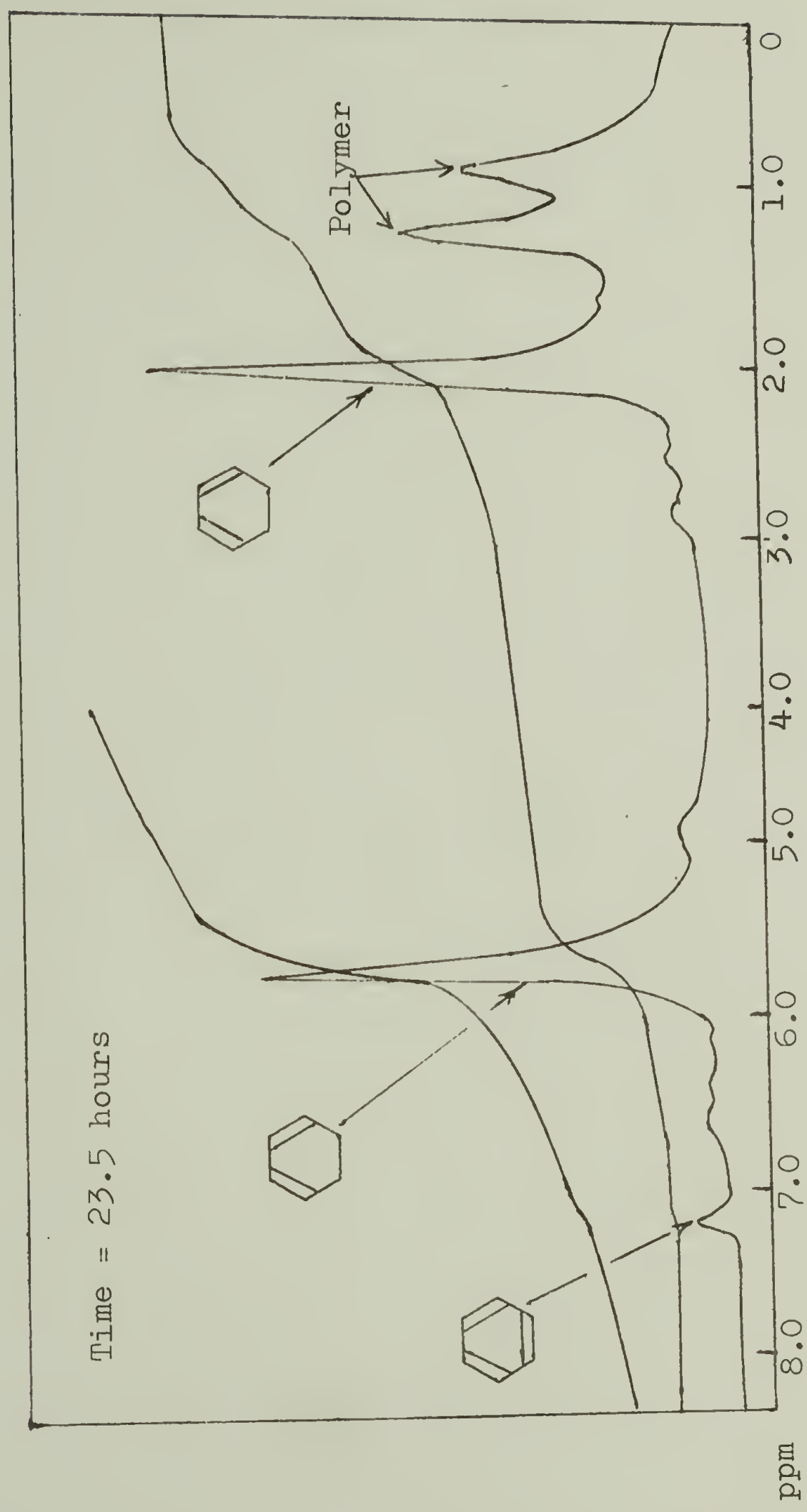


Figure D 1. Aromatization of 1,3-Cyclohexadienes during Anionic Polymerization.

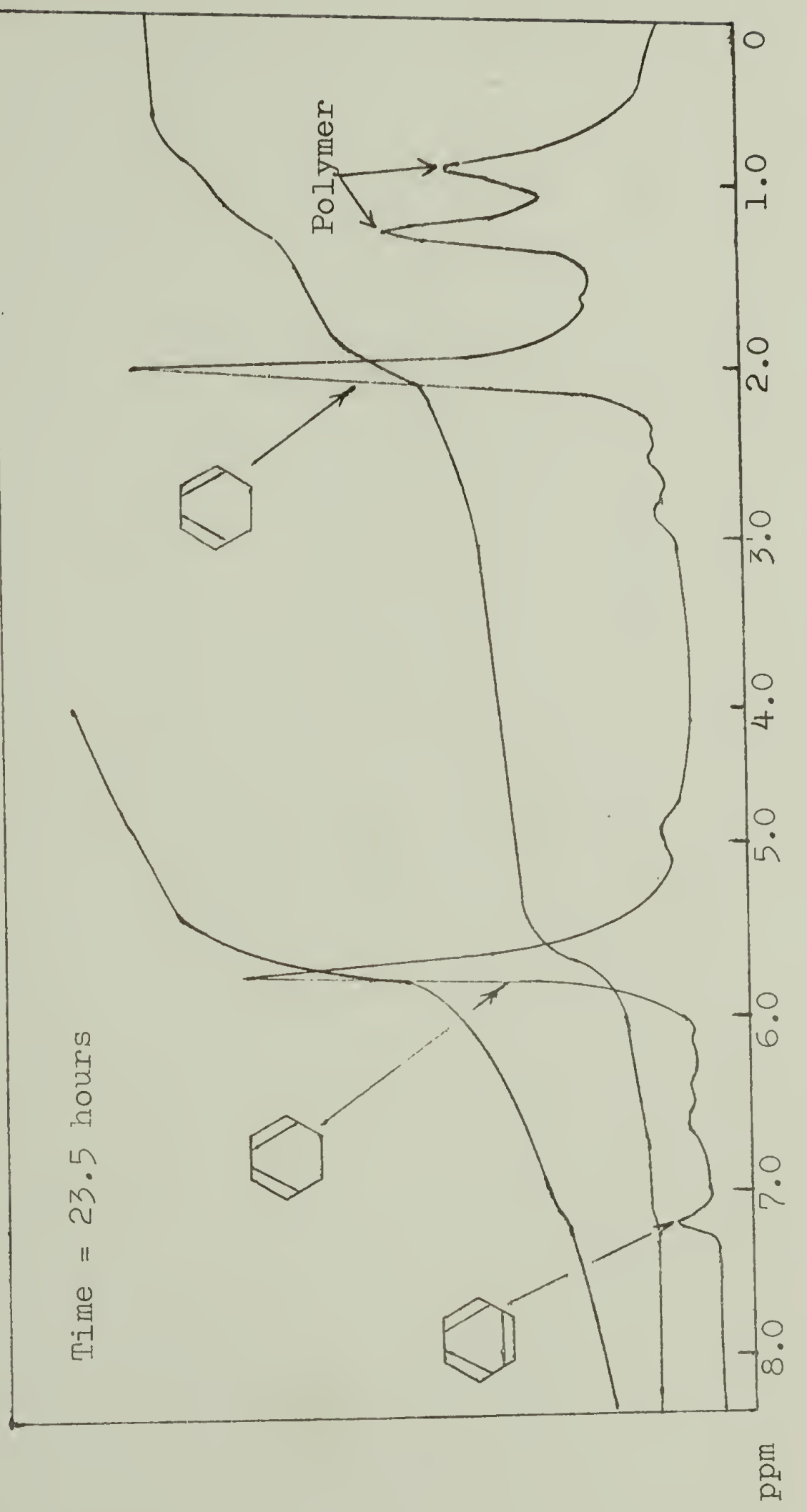


Figure D 1. Aromatization of 1,3-Cyclohexadienes during Anionic Polymerization.

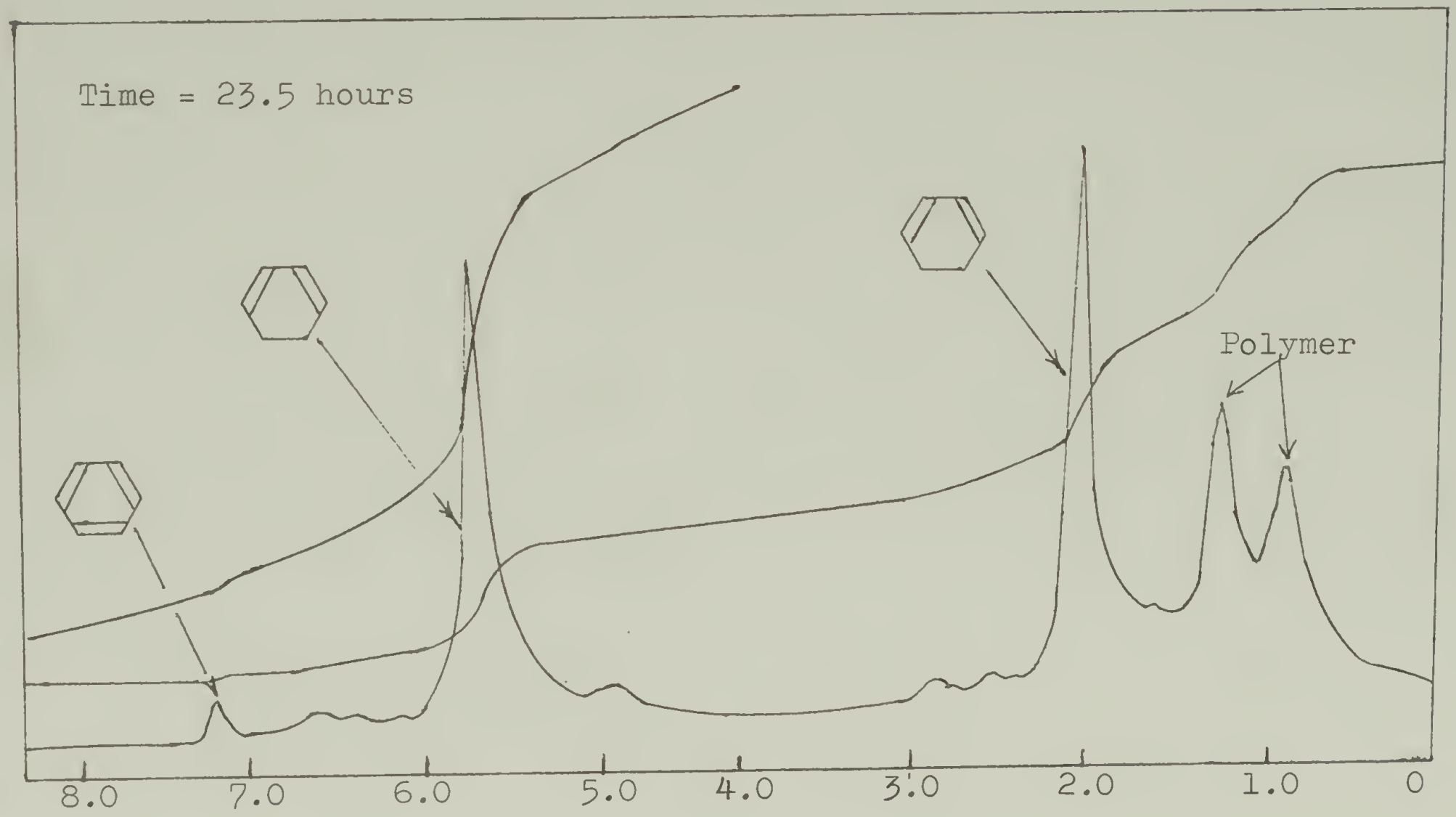
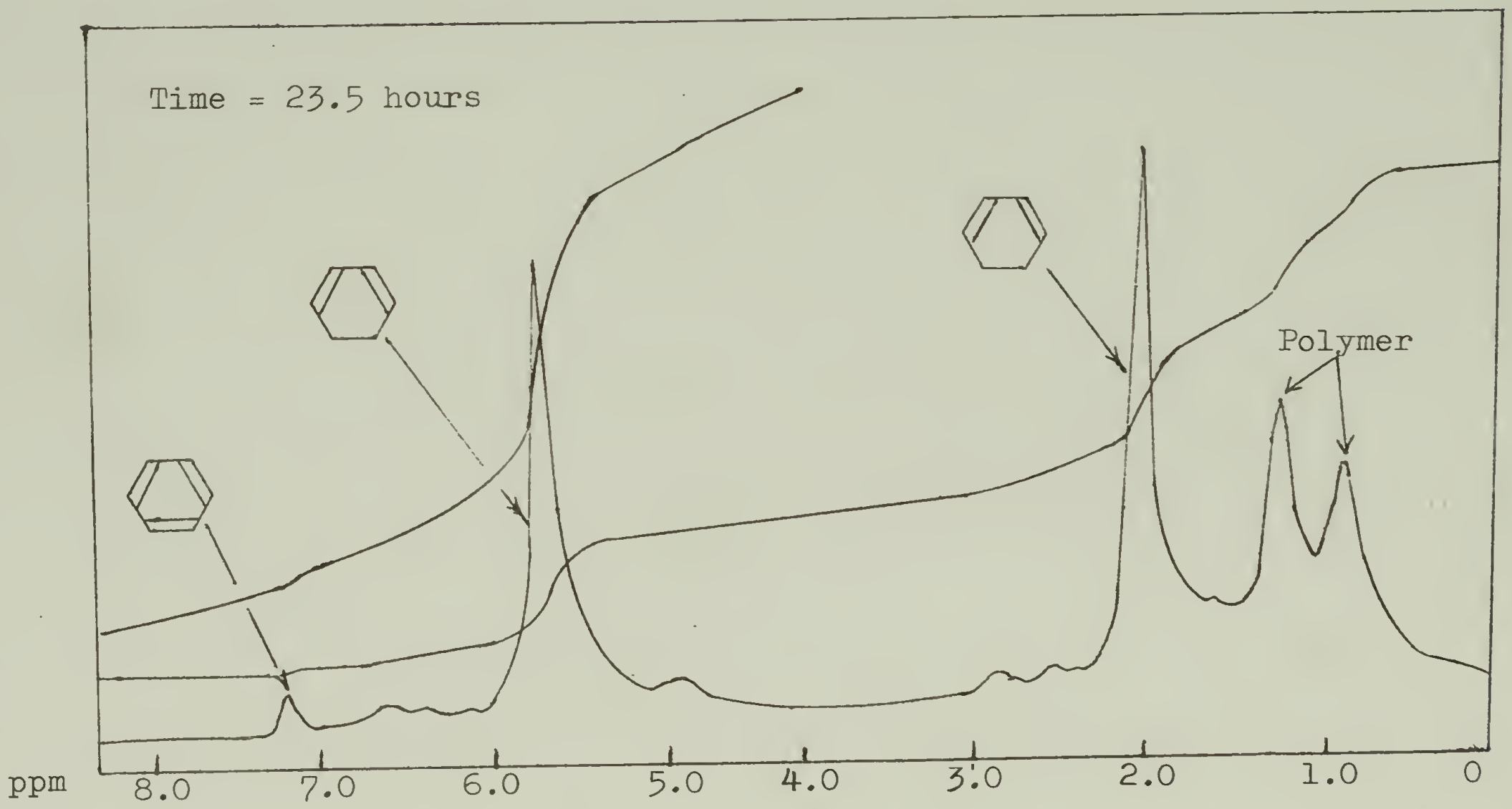


Figure D 1. Aromatization of 1,3-Cyclohexadienes during Anionic Polymerization.



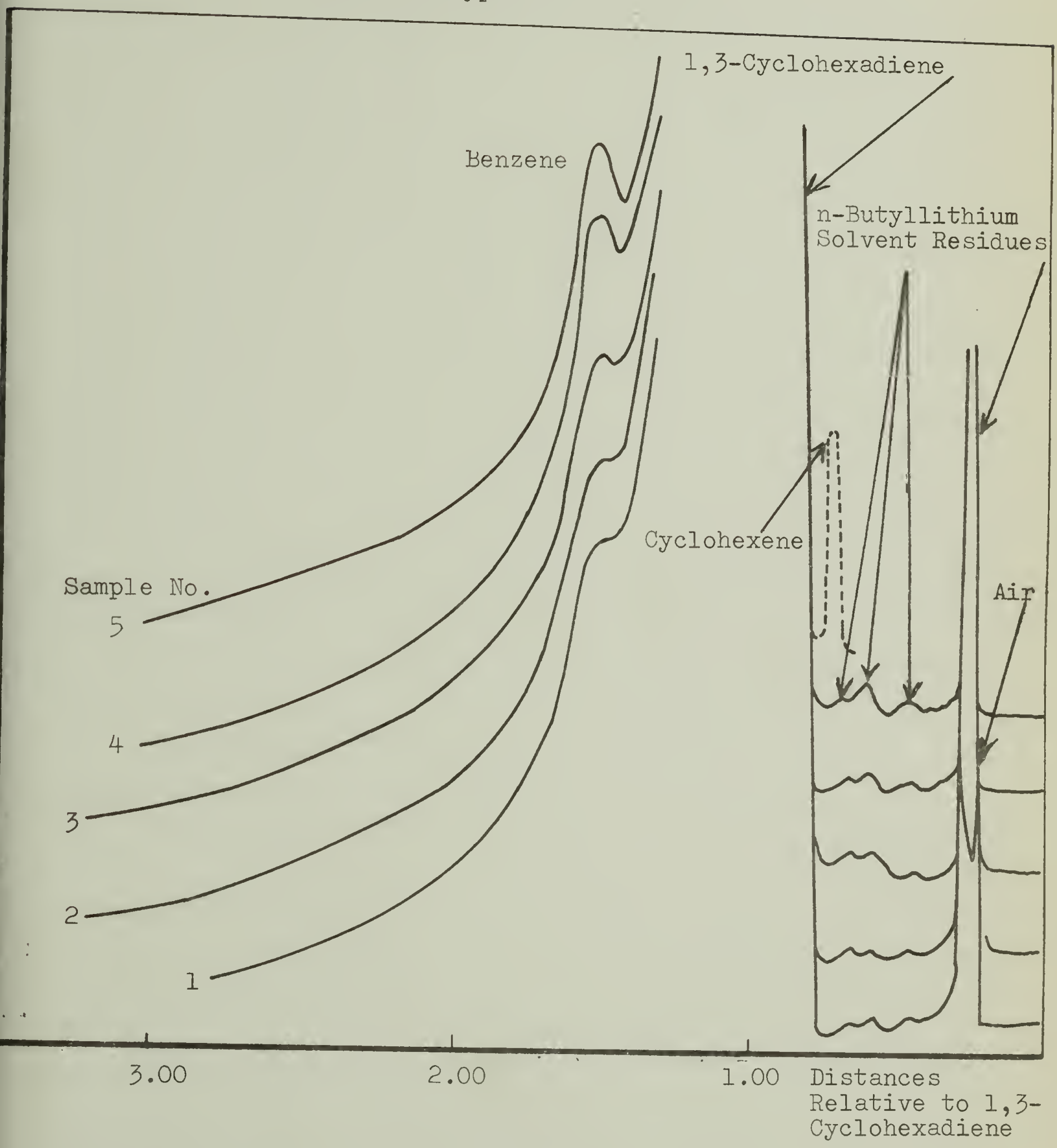
Two comments are relevant. On the basis of nmr alone it is not possible to establish if n-butyllithium, the polymeric carbanion, or both cause allylic abstraction. Secondly, the extent of abstraction is much less pronounced than in the case of 1,4-CHD and therefore, the magnitude of change approaches the detection limits of the nmr.

To substantiate the nmr findings a gas chromatographic experiment was performed (pp 99-100). At some point midway in an anionic bulk polymerization of 1,3-CHD with n-butyllithium, residual liquid monomer and any reaction byproducts were isolated by vacuum distillation from the non-volatile polymer and initiator. This mixture was analyzed by gas chromatography for changes in the benzene content as a function of time. The results are given in Figure D3. Peaks were identified by comparison with the retention times of known materials.

The results support the conclusion of the previous nmr experiment that benzene is formed as a byproduct during anionic polymerization of 1,3-CHD, and this in turn is apparently indicative of the formation and aromatization of cyclohexadienyl carbanions by abstraction of allylic protons from the monomer by the polymeric carbanion.

A significant question remaining is whether some of the proposed cyclohexadienyl carbanion reinitiates polymerization or all of it immediately aromatizes to (inert)

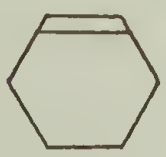
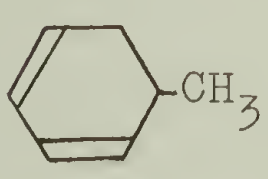
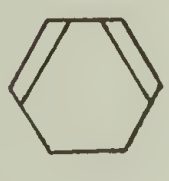
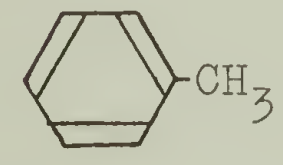
Figure D 3. Gas Chromatograms of Polymerization Reaction Byproducts.



benzene and lithium hydride. Reference to the ultraviolet adsorbance properties of structurally related low molecular weight compounds (Table D1) indicates that the residual

TABLE D1

ULTRAVIOLET PROPERTIES OF LOW MOLECULAR WEIGHT MODEL COMPOUNDS

Compound	λ(mμ) max	ε	Solvent	Reference
	207	450	MeOH	6; p. C259
	259	4,900	MeOH	6; p. C254
	260	10,000	MeOH	8
	λ / ε: 268 / 211; 264 / 150; 261 / 226	λ / ε: 259.5 / 188.0; 255.0 / 166.5; 253.5 / 154.0		7; p. 155

double bonds of the polymer should adsorb weakly in the range less than 210 mμ. However, the potential terminal diene unit should exhibit an intense adsorbance around 250-260 mμ. These adsorbances are sufficiently separated

to be easily distinguishable in the ultraviolet spectrum. Further, the molecular weights of the polymer samples of interest were sufficiently low to allow an adsorbance due to cyclohexadiene endgroups to be readily detected (Table E4).

Table D2 summarizes the adsorbance behavior which would be anticipated for these conditions if various

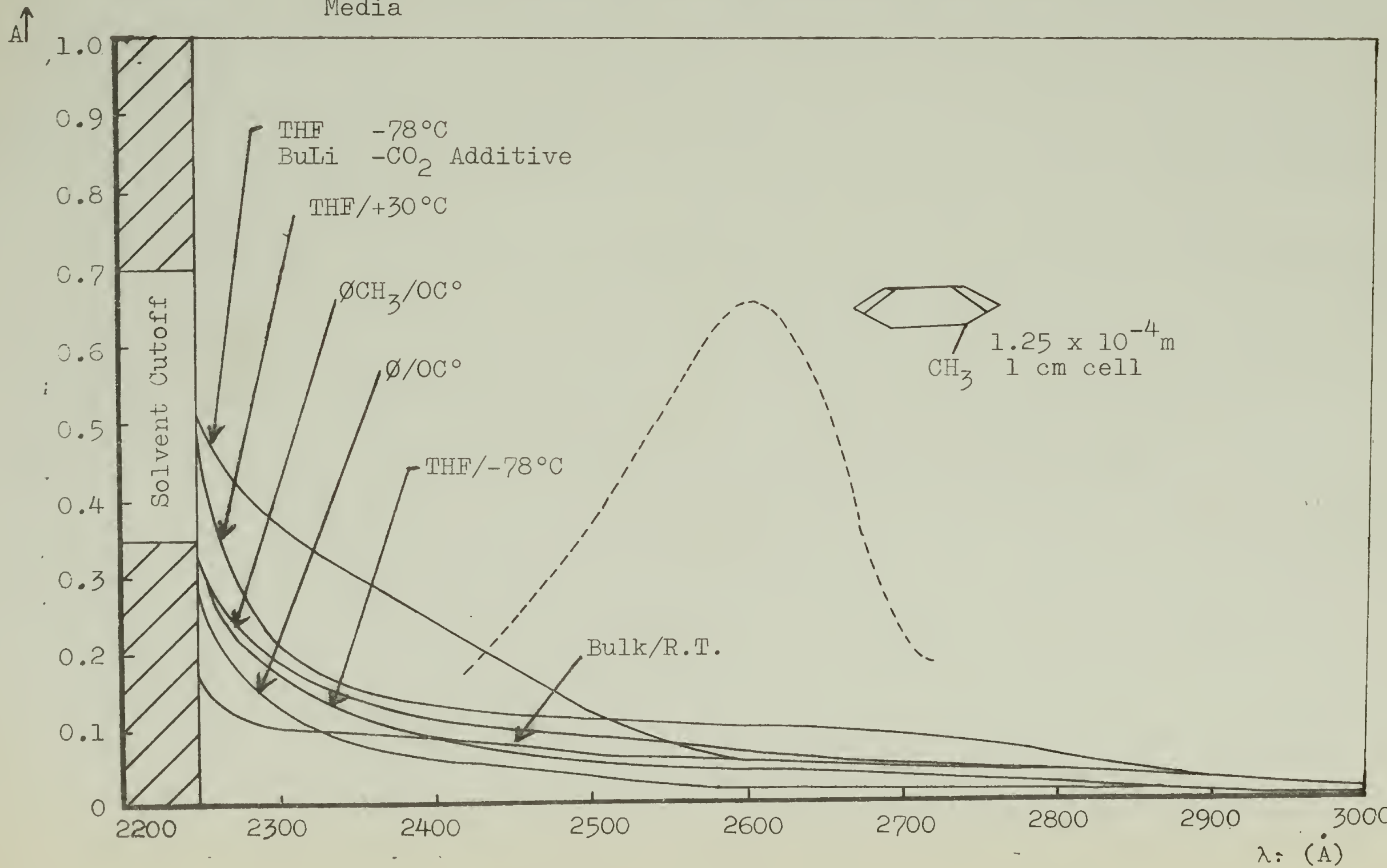
TABLE D2

ANTICIPATED ABSORBANCE BEHAVIOR AT 259 mμ FOR POLYMERS CONTAINING CYCLOHEXADIENYL OR PHENYL TERMINAL GROUPS

% of Endgroup	Anticipated for Cyclohexadienyl		Anticipated for Phenyl	
	M_n=5000	10,000	5000	10,000
100	1.47	0.735	0.0675	0.034
50	0.735	0.367	0.034	0.017
25	0.367	0.184	0.017	nil
10	0.147	0.0735	nil	nil

1. assumes sample sizes of 1.5 gm/l using 1 cm sample cells
2. for 0.02M solution of cyclohexene, expect A_{207} mu = 10. Explains observed upward curvature of spectra (in Figure D4) beginning at 220 mu.

Figure D 4. Ultraviolet Spectra of Polycyclohexadienes Synthesized in Various Media



amounts of polymer chains were terminated with cyclodiene units. These figures indicate it should have been possible to detect a level of 5% of the chains present being terminated with one cyclohexadiene unit. The samples studied included polymers synthesized under polar, non-polar and bulk conditions. Resulting ultraviolet traces as presented in Figure D4 indicate that no adsorbance due to terminal diene units was present. Apparently, therefore, chain reinitiation does not occur from anions formed during allylic abstraction. Here, it might be mentioned it is generally a more stringent test, especially in ultraviolet analysis with polymeric substrates, to demonstrate an observed lack of adsorbance.

The conclusion to this present work is summarized in Figure D5a,b which depicts molecular weight and conversion limitation by chain transfer to monomer by either a concerted or two-step mechanism. Essential features include formation of a cyclohexadienyl carbanion which immediately loses lithium hydride and aromatizes. It is noted that normal propagation requires seriously hindered steric contacts between the methylene groups of the monomer and the active endgroup. The allylic abstraction process which facilely occurs for this monomer in the presence of bases is considered to be a natural alternative to polymerization. In this regard, it is noteworthy that 1,4-CHD does not

FIGURE D 5a. Termination by Allylic Abstraction in Non-Polar Media via a Concerted Process.

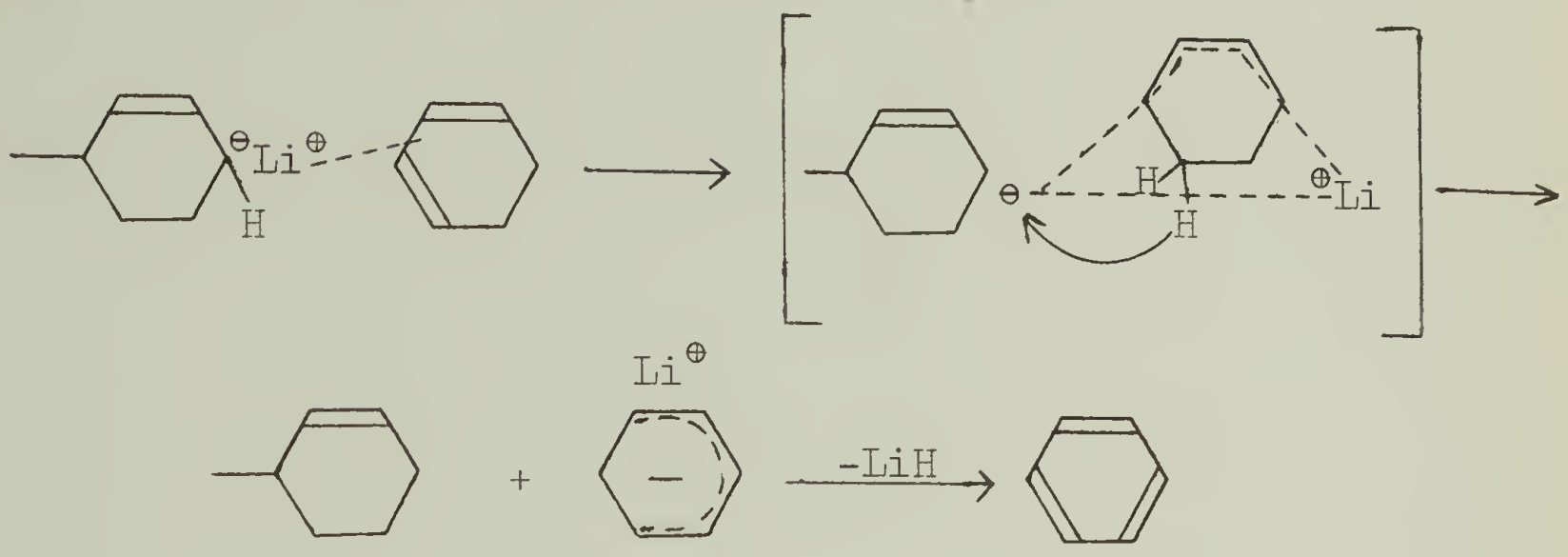
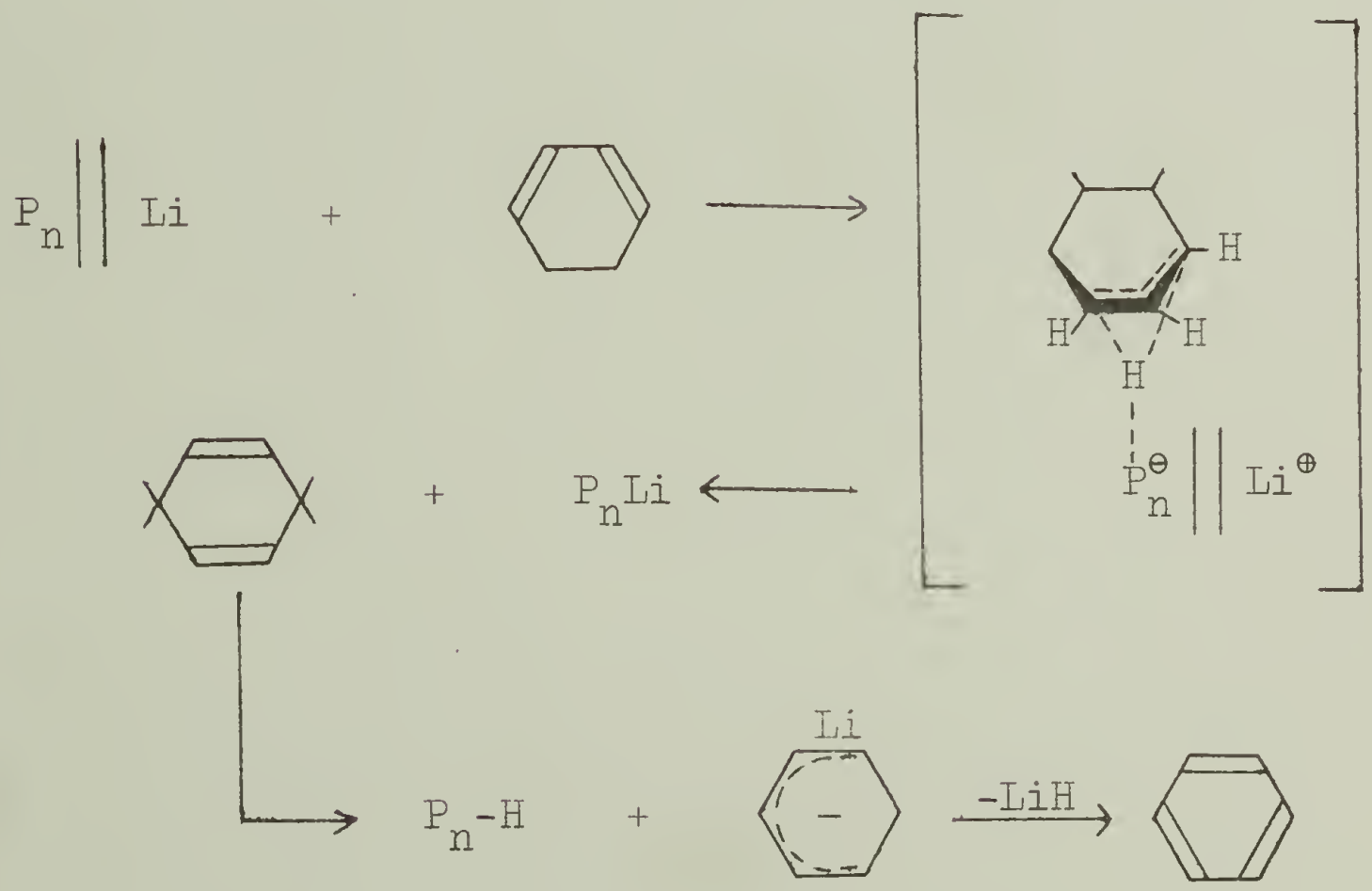


FIGURE D 5b. Termination by Allylic Abstraction in Polar Media via a Two Step Mechanism.



homopolymerize and is an effective chain transfer agent in 1,3-CHD polymerization.

This behavior suggests an important hypothesis concerning the behavior of cyclohexadiene systems in anionic polymerization. The distribution between allylic abstraction and addition (propagation) for the isomers is defined in a general way by the thermodynamics of both the abstraction and addition reactions which may occur for each isomer. In the case of allylic abstraction, since the same incipient anion is generated from both dienes, differences in the energy of the ground states should define the equilibrium concentration of the intermediate allylic anion (i.e., recall differences in the "steady state" approximation for free radical polymerization) which will be formed at given concentrations of diene and carbanions. For the cyclohexadienes, the 1,4-isomer is 580 cal/mole less stabilized in the ground state than the conjugated (1,3) isomer (p 9). Using a simple Arrhenius-type calculation indicates the concentration of cyclohexadienyl anion generated from a given concentration of 1,4-CHD and base (polymeric carbanion) should be roughly twice the anion concentration resulting from a similar 1,3-isomer conc. Hence, 1,4-CHD should be approximately twice as likely as the 1,3-isomer to partake in the allylic abstraction sequence leading to termination. This difference, however, is not sufficient

to account for the complete lack of polymerizability of 1,4-CHD by anionic methods. Thus, one might deduce that the major factor governing the much higher $k_{transfer}/k_{propagation}$ for 1,4-CHD is the lower reactivity of the 1,4 compound to carbanionic addition when compared to the 1,3-isomer.

II. Stereochemistry of Polycyclohexadienes

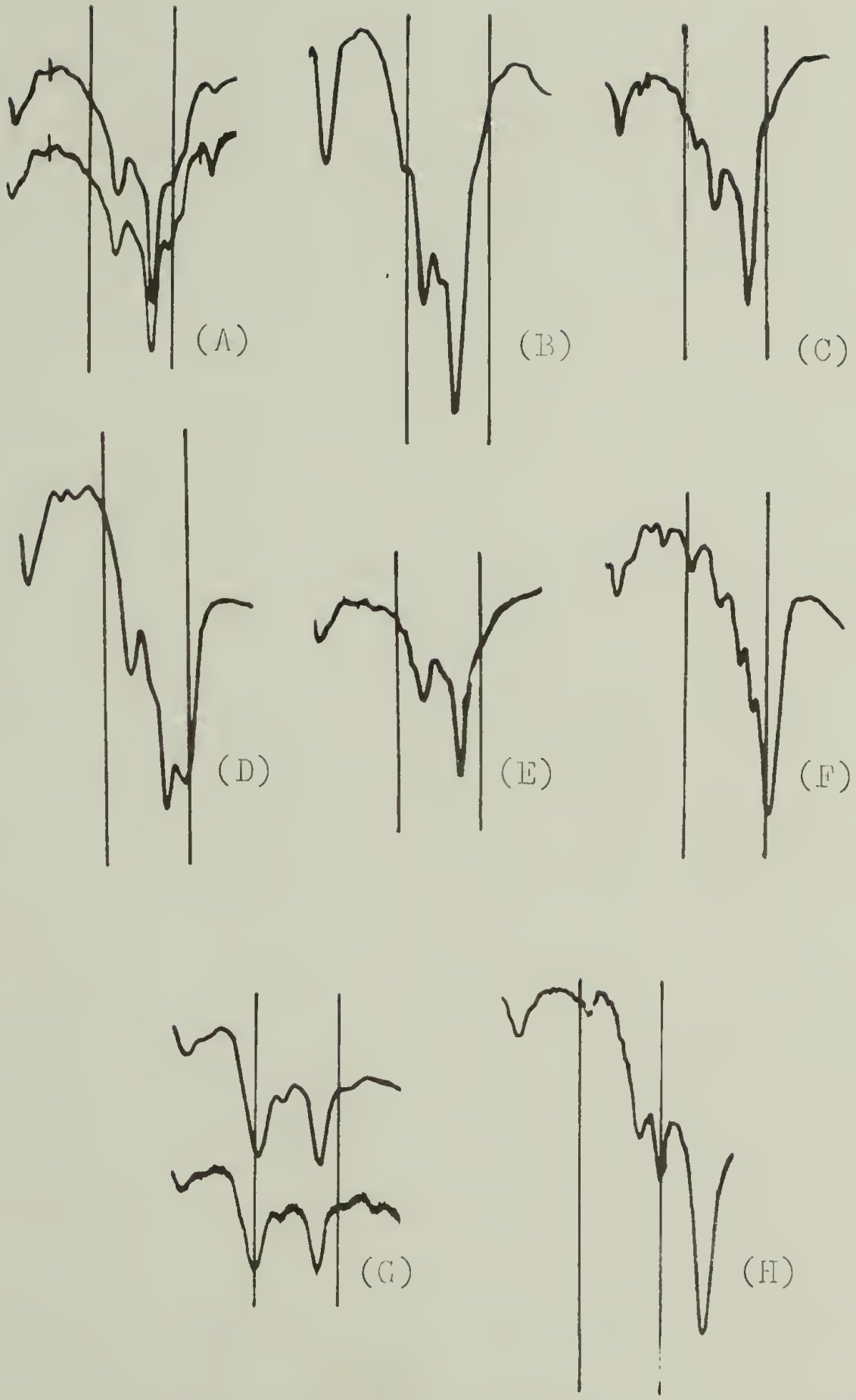
A. Introduction. Extensive, and oftentimes elegant work has been done to relate poly-diene microstructures to reaction conditions and monomer structure and to rationalize the observed empirical relationships in terms of one overall mechanistic concept (87,88,89). In this regard, the effect, on microstructure, of having the diene center present in an unstrained ring system (i.e., 1,3-CHD) has not been examined in detail and represents a gap in the current state of this type of information.

Being a cyclic diene, the residual double bond of 1,3-cyclohexadiene after polymerization must remain in a cis configuration. Also, the ring methylene groups of the ultimate chain unit and the incoming monomer will be in close proximity to the reaction center and might be expected to exert an important influence on the resultant microstructure.

Polycyclohexadiene exhibits a potentially complicated microstructure (pp 34-39) characterized by 1,2 vs. 1,4 addition, cis vs. trans ring insertion and a varied tacticity. The methods developed and used to determine these structural parameters are described in this section and the results are interpreted on the basis of a postulated mechanism.

B. 1,2 vs. 1,4 addition. Background. Polycyclohexadiene consists of a series of cyclohexene rings wherein the residual double bond occurring in a six member ring is locked into a cis conformation. Such disubstituted cis olefin structures exhibit an adsorption in the infrared region for C-H out-of-plane hydrogen deformations near 700 cm^{-1} (94). Simple hydrocarbon derivatives of ethylene (Table D3) absorb over a range of 675-730 cm^{-1}, and cyclohexene, a model for polycyclohexadiene, adsorbs at 721 cm^{-1} (IR 9). This variable cis olefin adsorption holds true for polymers; cis-1,4-polybutadiene exhibits general absorbance over a range 650 to 800 cm^{-1} which is assigned to such olefin out-of-plane deformations (95).

In the case of polycyclohexadienes synthesized in a variety of media (IR 22, p 178) general adsorption was observed between 650-800 cm^{-1} in the infrared spectra (IR 17) and assigned to C-H out-of-plane hydrogen deformations on the basis of the above background information.



IR-22. C-H out-of-plane deformation bands for polycyclohexadienes synthesized in various solvent media; 625 to 900 cm^{-1} region of the infrared spectrum.

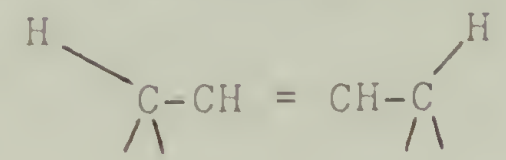
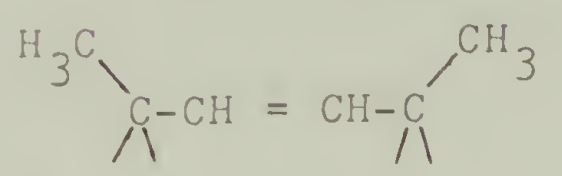
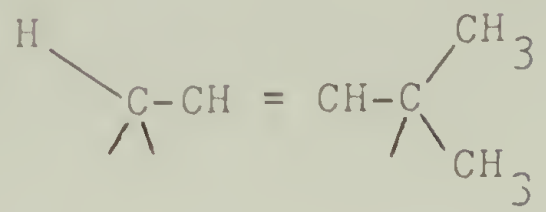
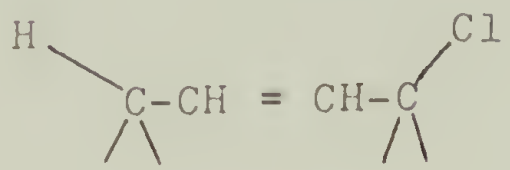
Support for this assignment occurs in the absence of adsorbance in this region for samples which were quantitatively hydrogenated to polycyclohexane (IR 18); this apparently links the origin of the 650-800 cm^{-1} bands to olefin content in the precursor polymer. We have attempted to interpret the multiple adsorbance between 650-800 cm^{-1} in the polycyclohexadiene spectra in terms of the 1,2 vs. 1,4 content of the polymers.

Model compound studies. An essential feature of the olefin C-H deformation near 700 cm^{-1} is its sensitivity (and hence, potential utility) to adjacent molecular structure. In simple straight-chain olefins, substitution of chlorine, methyl or an oxygenated group at the α-position, results in a marked shift in the C-H deformation band to higher frequences (97,98,99). In Table D3, cis-2-butene, having no branching at the α-carbon adsorbs at 675 cm^{-1}. Addition of an alkyl branch at the α-carbon, such as $-CH_3$ or $-CH_2CH_3$, shifts this band to 709 cm^{-1}. Two alkyl groups, as in 4-methyl-cis-2 pentene, shifts this band another 10 cm^{-1} to 719 cm^{-1}. Similar behavior occurs for chlorinated olefins. The 675 cm^{-1} adsorption for cis-2-butene is shifted to 769 and 787 cm^{-1} with the addition of one and two chlorine "branches" respectively.

In the present study, a series of dimethylcyclohexenes (pp 71-73, 107-109) had their infrared spectra determined

TABLE D3,4

VARIANCE OF THE CARBON-HYDROGEN OUT-OF-PLANE VIBRATION BANDS AS A FUNCTION OF ADJACENT MOLECULAR STRUCTURE

Compound	Structure	C-H(cm^{-1})
D3 Alicyclic Olefins		
a. 2-butene		675
b. 3-hexene		709
c. 4-methyl-2-pentene		719
d. 1-chloro-2-butene		769

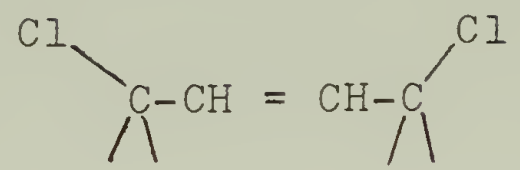
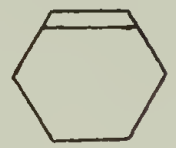
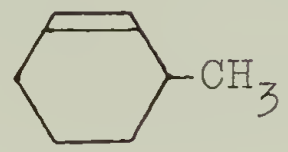
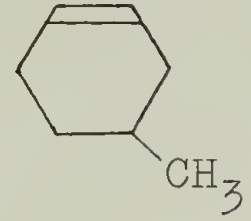
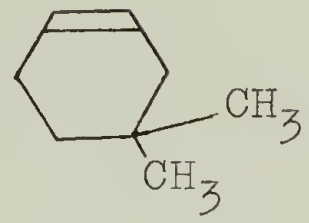
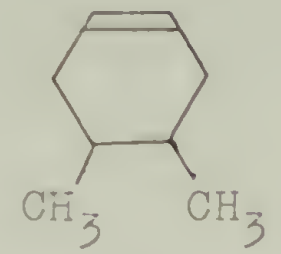
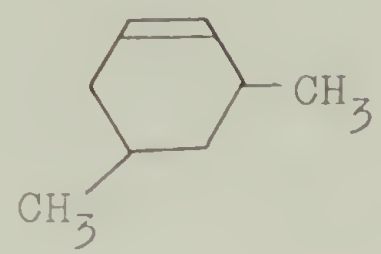
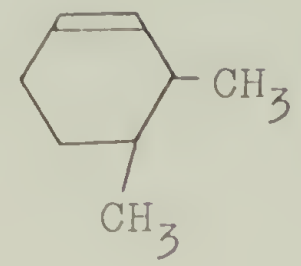
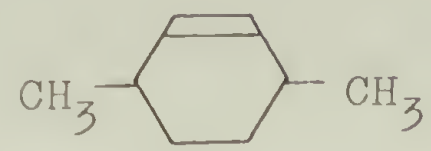
e.	1,4-dichloro-2-butene		787
	D4 Cyclic Olefins		
a.	cyclohexene		726
b.	3-methylcyclohexene		717-23
c.	4-methylcyclohexene		720-25
d.	4,4-dimethylcyclohexene		759

TABLE D3,4--Continued

Compound	Structure	C-H(cm^{-1})
e. 4,5-dimethylcyclohexene		758 (712)[a]
f. 3,5-dimethylcyclohexene		720
g. 3,4-dimethycyclohexene		750; 783
h. 3,6-dimethylcyclohexene		783;802

[a]Two strong bands were observed at 712 and 758 cm^{-1}; the band at 758 cm^{-1} was the preferred assignment since it was considered unlikely this substituted derivative should adsorb at a frequency (i.e., 712 cm^{-1}) less than 725 cm^{-1}, for unsubstituted cyclohexene.

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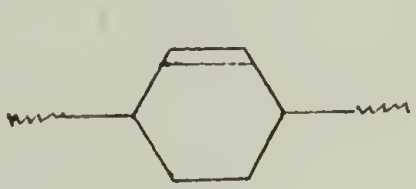
to verify if the behavior of simple olefins above extends to more complex cyclo-olefin systems. The results are summarized in Table D4. The infrared spectra of cyclohexane (IR 8) and the corresponding dimethylcyclohexanes (IR 14a,f) indicate there are no absorptions in the region from 625 to 800 cm^{-1} for the concentration conditions used. Thus, the bands referred to in the table are apparently related to the C-H olefin deformation bands.

In attempting to develop a structure vs. adsorbance correlation, cyclohexene, being the simplest and least branched compound of the set, was chosen as the reference compound. This material adsorbs at 726 cm^{-1}. A single methyl branch at the α-or β-position, as in D4b,c, apparently does little to vary the position of this band. Two methyl branches, however, shift the band to frequencies as high as 800 cm^{-1} (D4d-h). Thus, disubstitution on one or both β-carbons (D4d,e) gives a value near 760 cm^{-1}. Location of this methyl branching at the alpha position and nearer the olefin center enhances this shift still further. 3,4-Dimethylcyclohexene (D4g) possessing one α- and one β-methyl group adsorbs at 750 and 783 cm^{-1}, while 3,6-dimethylcyclohexene (D4h), with both methyl groups occurring as branches, adsorbs at 783 and 802 cm^{-1}. However, 3,5-dimethylcyclohexene (D4f), with one α- and

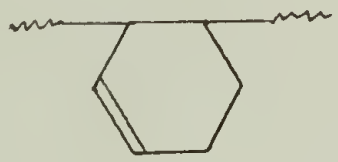
one β-methyl group, adsorbs at 720 cm^{-1}, a value considerably less than that expected on the basis of the trend thought to be exhibited by the other members of the series.

A good explanation for this apparent anomaly is not known at this time. Nevertheless, it seems qualitatively true that methyl disubstitution at the α-and β-carbons in cyclohexene does shift the C-H deformation band from 726 cm^{-1} to 800 cm^{-1} in general agreement with the results previously observed for open chain olefins.

3. Relation to polymer microstructure. In common with polymers derived from diene monomers generally, polycyclohexadiene may exhibit structural isomerism (1,2 or 1,4 addition).



1,4 addition



1,2 addition

1,2 Addition results in the cyclohexene repeating unit being branched (by adjacent repeating units) once at each α-and β-carbon atom. 1,4 Addition results in branching once at each of the α-carbon atoms. Utilizing the adsorbance behavior exhibited by low molecular weight olefins as a guide, it was anticipated that the 1,4 units might produce general adsorbance around 775-800 cm^{-1} while

adsorbance due to the 1,2 units would appear at lower frequencies in the region 720-775 cm^{-1}.

To test this, a set of polycyclohexadienes was synthesized under various reaction conditions and their infrared spectra determined for the region 900-625 cm^{-1}. The results are summarized in Table D5; band positions are accurate to $\pm$ 2.5 cm^{-1}.

In the polycyclohexadiene spectra, at least five bands were observed in the 690-800 cm^{-1} region. The bands are overlapped so that the apparent peak maxima might not correspond to the actual maxima. For this reason, and because the relative extinction coefficients are not known, the results of Table D5 are given on the basis of whether a band is present (+) or a band is absent (-). All the polymer spectra exhibit strong bands at 721-23 cm^{-1} and 760-65 cm^{-1} independent of reaction conditions. For polymers synthesized in non-polar media (benzene, toluene, bulk) additional, bands were observed at 785 and 800 cm^{-1}. In such media, presumably tight ion-pair propagation occurs in anionic polymerization of diene monomers, and this state is known to favor 1,4 addition in open-chain dienes (87).

Assignment of these bands to 1,4-addition would also be consistent with the previous model compound behavior. It was predicted that 1,4 addition, which gives the most

TABLE D5

VARIANCE OF CARBON-HYDROGEN OUT-OF-PLANE DEFORMATIONS IN POLYCYCLOHEXADIENES AS A FUNCTION OF REACTION CONDITIONS

Synthetic Conditions	Apparent Band Mixima (cm^{-1})					
	795-800	780-785	760-765	740sh	720-725	690 700sh
THF						
-78°	-	-	+	-	+	+
0°	-	-	+	-	+	+
25°	-	-	+	-	+	+
ØCH$_3$						
-78°	+	+	+	-	+	+
0°	+	+	+	-	+	+
25°	+	+	+	-	+	+
Ø						
0°	+	+	+	-	+	?
Bulk						
RT	+	+	+	+(small)	+	?
n-Hexane						
w/TMEDA	-	-	+	+	+	+
w/THF(98/2:n-hexane/THF)	-	-	+	-	+	?
THF						
w/Buli/CO_2	same as THF alone					
Ziegler-Natta						
VCl_3	+	-	+	-	+	?
$TiCl_4$ w/$(isoBu)_3Al$	-	-	-	-	+	+

α-carbon branching in the repeating units, would be characterized by the highest frequencies observed for C-H deformation vibrations. Support for this expectation was found by observing the effect on the infrared spectra of polycyclohexadienes synthesized in the presence of polar additives in non-polar media. When solvating additives such as 2% tetrahydrofuran, TMEDA (1/1 mole ratio to n-butyllithium) are added to polymerizations taking place in hexane, the bands at 785 and 800 cm^{-1} associated with 1,4 addition are absent. Apparently, solvation or complexation interferes with the tight ion-pair formation and resulting counterion-monomer association needed for 1,4 addition.

Synthesis in polar media, or in the presence of solvating agents produced spectra which exhibited only two strong infrared bands at 720 and 765 cm^{-1}. In the anionic polymerization of other dienes, high and sometimes exclusive 1,2-addition was favored in such media (87). Therefore, assignment of the 720 and 765 cm^{-1} bands to 1,2-addition was consistent with this reported behavior. Also, this assignment is in accord with the model compound results which predicted that 1,2-addition, resulting in substitution at the positions α and β to the residual olefin bond, should be characterized by C-H deformation

band frequencies less than those associated with 1,4 addition.

In summary, the bands at 785 and 800 cm^{-1} have been assigned to 1,4-addition while the pair at 721 cm^{-1} and 765 cm^{-1} were assigned to 1,2-addition. Synthesis in polar media or in the presence of solvating additives gave virtually exclusive 1,2-addition. The use of non-polar conditions caused partial 1,4-content to be formed but predominate (about 80-90% of the total area under the peaks in the 675-800 cm^{-1} region) 1,2-content remains. This assertion would represent an unusual feature of 1,3-CHD polymerization and a possible mechanistic interpretation is suggested in the next section.

C. Cis vs. trans ring placement. The nmr and infrared techniques which are most often used to characterize polymer microstructure seem to be insensitive to the relative amounts of cis vs. trans ring placement in the case of polycyclohexadiene. The nmr spectra of polycyclohexadienes synthesized in a variety of media all exhibit two broad, featureless, overlapping peaks at 1.6 and 2.0 ppm for the aliphatic protons (NMR-1) while bands in the infrared spectra cannot be unambigously assigned to cis vs. trans ring placement (IR-17). An indirect solution to this problem has been attempted. The nmr spectra of

disubstituted (e.g., methyl, hydroxyl, acetoxy) cyclohexanes exhibit strikingly characteristic resonance patterns for the ring methylene protons depending upon the cis vs. trans placement of the substitutents (see later discussion). Such compounds may be considered structurally similar models of the repeating units which would exist upon quantitative hydrogenation of polycyclohexadiene to polycyclohexane.

The nmr spectra of isomerically pure cis- and trans-1,2-and 1,4-dimethylcyclohexanes are given in Appendix 3 (NMR-4-7). For both cis isomers, the resonances for the ring protons are observed as a single, sharp peak located at 1.40 ppm., while the trans isomer exhibits a series of overlapped peaks centered at roughly 1.65 ppm. (Table D6).

TABLE D6

RING PROTON PEAK WIDTHS FOR DIMETHYL-CYCLOHEXANES (90)

Dimethylcyclohexane	Peak Widths(cycles/sec) at Half Heights
1,2-cis	4.8
1,2-trans	14.1
1,3-cis	12.8
1,3-trans	8.6
1,4-cis	4.8
1,4-trans	19.2

This behavior is believed to be caused by a combination of shielding effects and the relative possibility of rapid interconversion of conformers (91). The equatorial and axial protons of cyclohexane resonate at 1.65 and 1.17 ppm, respectively (92). Placement of an equatorial methyl group shields adjacent equatorial protons by +0.28 ppm and adjacent axial protons by +0.47 ppm. Thus, trans-1,2-dimethylcyclohexane (and 1,4), which must have both of its methyl groups mostly in the diequatorial conformation, has a temperature independent spectrum (90) which exhibits a broad resonance for the ring protons. Alternately, an axial methyl group shields adjacent equatorial protons by +0.4 ppm and the four adjacent axial protons by -0.2 ppm. This causes the ring proton resonances to sharpen in cis-1,2-and 1,4-dimethylcyclohexane, where one methyl group is always in the axial position. In addition to this shielding effect, a rapid interconversion of equivalent conformers occurs for the cis isomer which causes averaging of axial and equatorial proton chemical shifts whereas in the trans isomer the conformation is essentially fixed. The net effect is the observed narrow resonance peak characteristic of the ring protons of the cis-1,2 and 1,4 isomers. This effect on peak width is not restricted to alkyl groups, but has also been observed for hydroxyl and

acetyl, etc. (93) groups.

In the present work on polymer microstructure, it was hoped that a similar effect in the nmr spectra would be observed for polycyclohexanes, where adjacent cyclohexane rings take the place of the methyl and other groups in the disubstituted cyclohexanes mentioned previously.

The results are given in Figure D6. It has been shown by a combination of infrared, nmr and elemental analysis that the polycyclohexadienes involved were essentially completely converted during hydrogenation to the corresponding polycyclohexanes (p 119,121). The synthetic conditions used to prepare the polycyclohexadienes before reduction are noted in the figure. When the original synthesis took place in non-polar, non-dissociating media (p 28), such as in benzene or in bulk, the corresponding polycyclohexadienes after hydrogenation exhibited a narrow resonance for the ring protons centered at 1.45 ppm, which is characteristic of predominantly cis ring placement. Synthesis of the diene polymer in polar media gives after hydrogenation of a polymer with a broad, ill-defined resonance for the ring protons located between 0.8 and 2.0 ppm, which is characteristic of predominantly trans ring placement.

Further support that increasing trans ring placement is related to endgroup solvation is found in Figure D6,

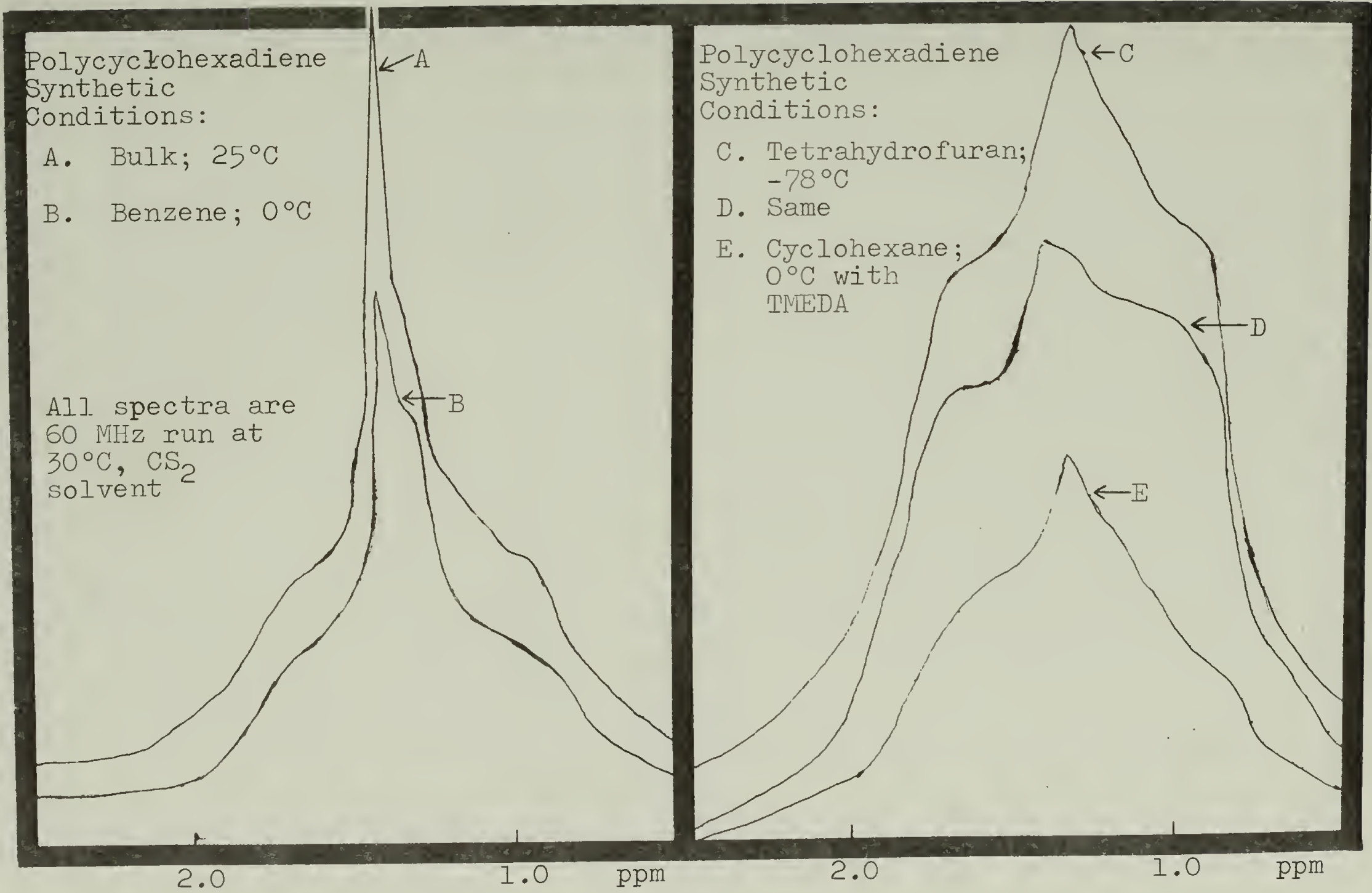


Figure D 6. Variance of the Ring Proton Resonances for Polycyclohexanes Derived from Polycyclohexadienes Synthesized in Various Media.

No. E. The polymer sample was synthesized in cyclohexane, a non-dissociating media, but nevertheless exhibited a high trans content on the basis of nmr when a mole equivalent of tetramethylethylenediamine (TMEDA) to n-butyllithium was added to the reaction mixture. the TMEDA is thought to complex in non-polar media with the lithium to permit free-ion propagation of the type associated with solvating media (82; p 510).

Because of the complexity of the spectra, the extent of cis vs. trans ring placement is not directly available from the nmr spectra. However, to make an estimate of cis/trans ratio, isomerically pure cis- and trans-1,2-dimethylcyclohexanes were mixed to form a series of samples varying in cis and trans content (p 112), and the nmr spectra of the resulting neat mixtures were obtained (Figure D7). The ring proton resonance peaks for these models were compared to those in the spectra of polycyclohexanes. Firstly, it is noteworthy that the sharp resonance peak for the ring protons in the cis isomer occurs at 1.41 ppm, which compares closely with the location of the sharp peak in the polymer spectra at 1.45 ppm. Secondly, comparison of peak geometries yields the semi-quantitative estimate that polycyclohexadienes synthesized in polar media contain almost complete trans ring placement

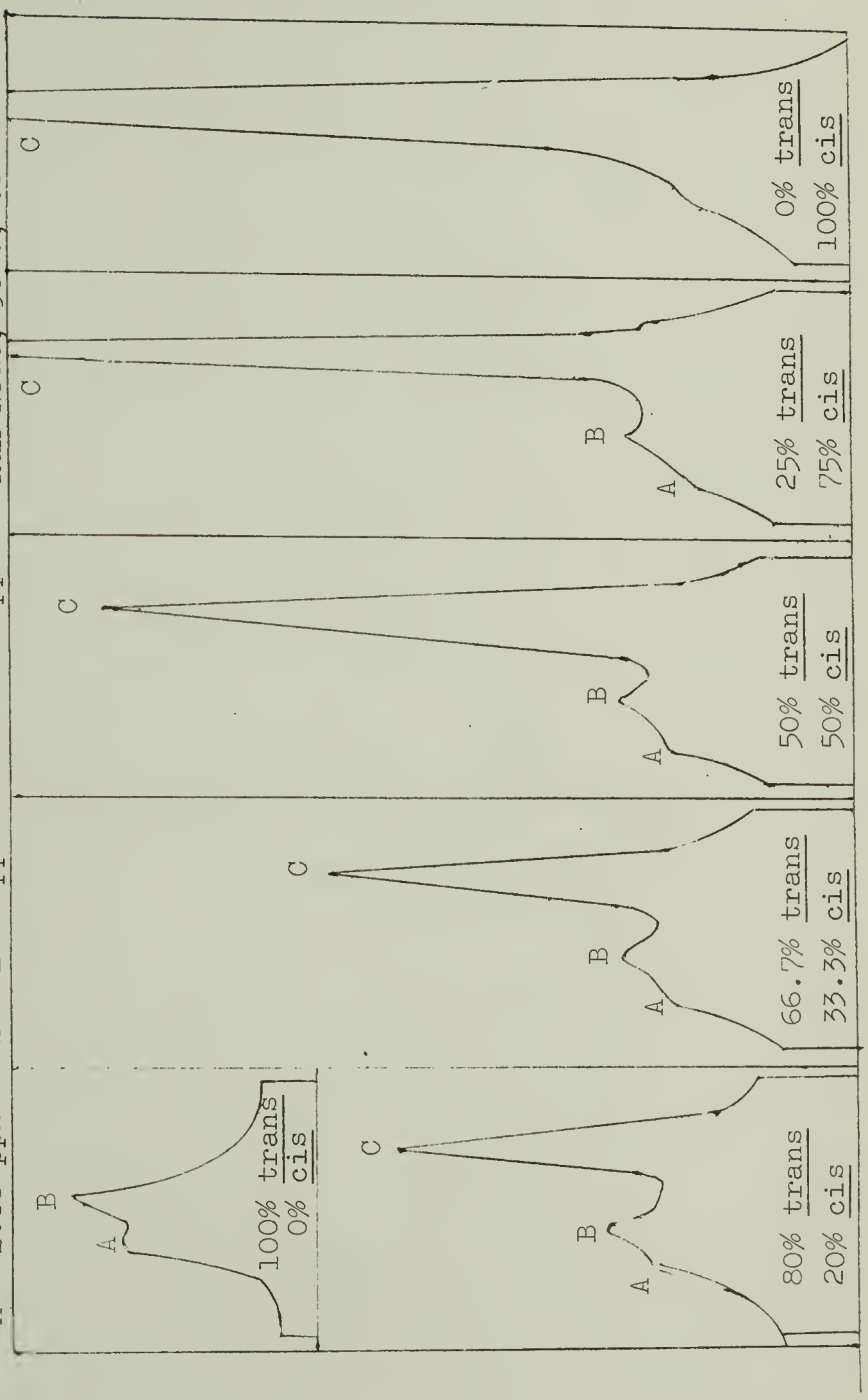


Figure D 7. Variance in the NMR Proton Resonance Pattern for the Ring Methylene Protons of 1,2-Dimethylcyclohexanes as a Function of cis-trans Ratio.

whereas synthesis in non-polar media gave greater than 75% cis ring placement. A mechanistic explanation is postulated in the following section.

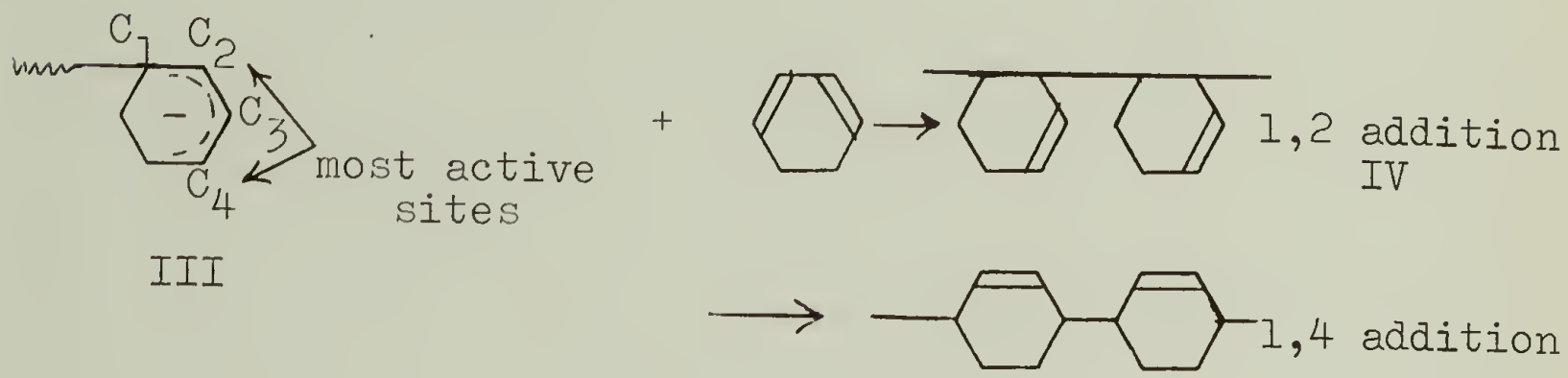
D. Sterochemistry of propagation in 1,3-CHD polymerization. The propagation mechanism for the anionic polymerization of 1,3-CHD must account for high 1,2-addition with trans ring placement in polar media, and predominantly 1,2-addition with some 1,4 content and cis ring placement in non-polar media. Explanations for this behavior are suggested in Figures D8 and D9.

In non-polar media, initial complexation of the diene with the counterion leads to a six center transition state (I) and insertion of the monomer between the counterion and chain end (II) to complete the 1,4-propagation (104;p 120). In the case of 1,3-CHD, this complexation would give a transition state which embodies repulsive steric contacts (8 VII) between the ring methylene groups on the chain endgroup and the monomer during the formation and insertion steps, as summarized previously. It is suggested this severe steric hindrance is overcome by an "off-center" complexation (VIII) which leads to insertion of the diene in a 1,2 fashion (IX).

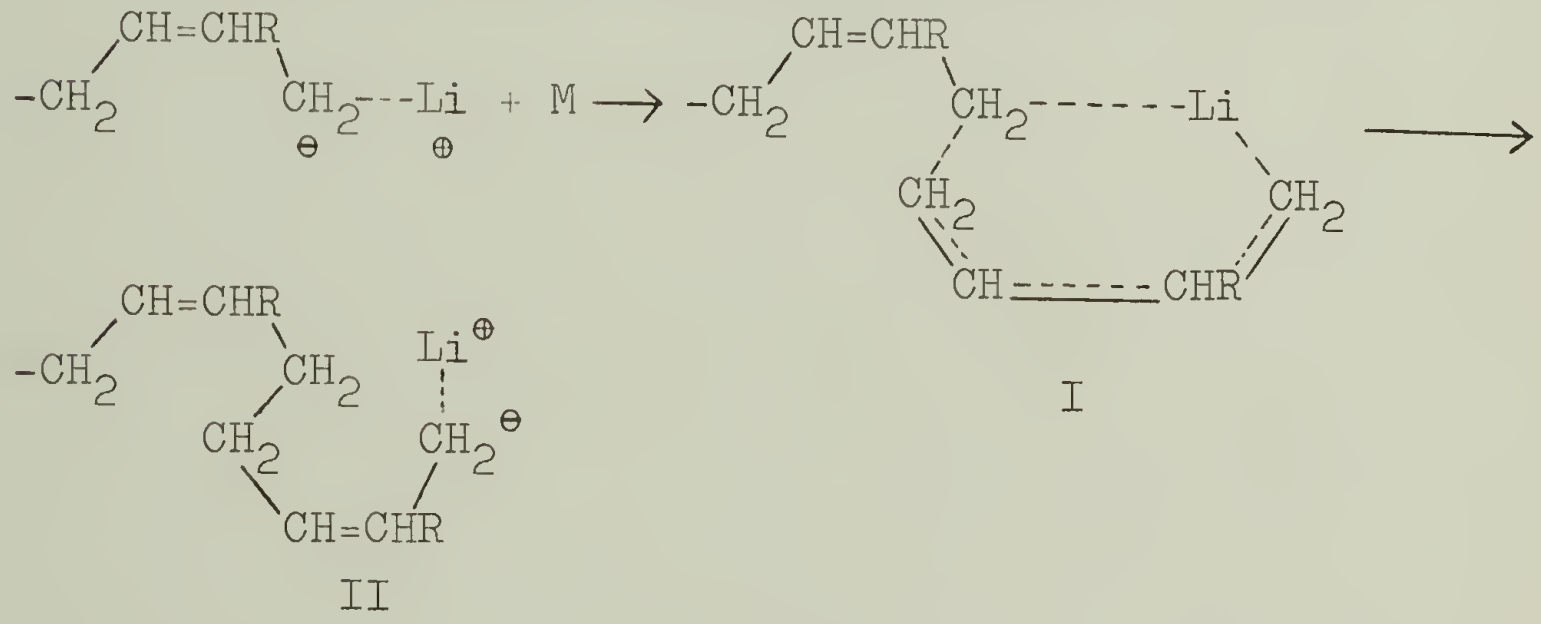
In polar media solvation leads to the π-allylic species (8 III) as the propagating center. In open chain

Figure D 8. 1,2 vs. 1,4 Addition in the Anionic Polymerization of 1,3-Cyclohexadiene.

A. Proposed Propagation Sequence for 1,3-Cyclohexadiene in Polar (Solvating) Media.



B. Presently Accepted Propagation Sequence for Anionically Polymerized Diene Monomers in Non-Polar Media.



C. Proposed Propagation Sequence for 1,3-CHD in Non-Polar Media.

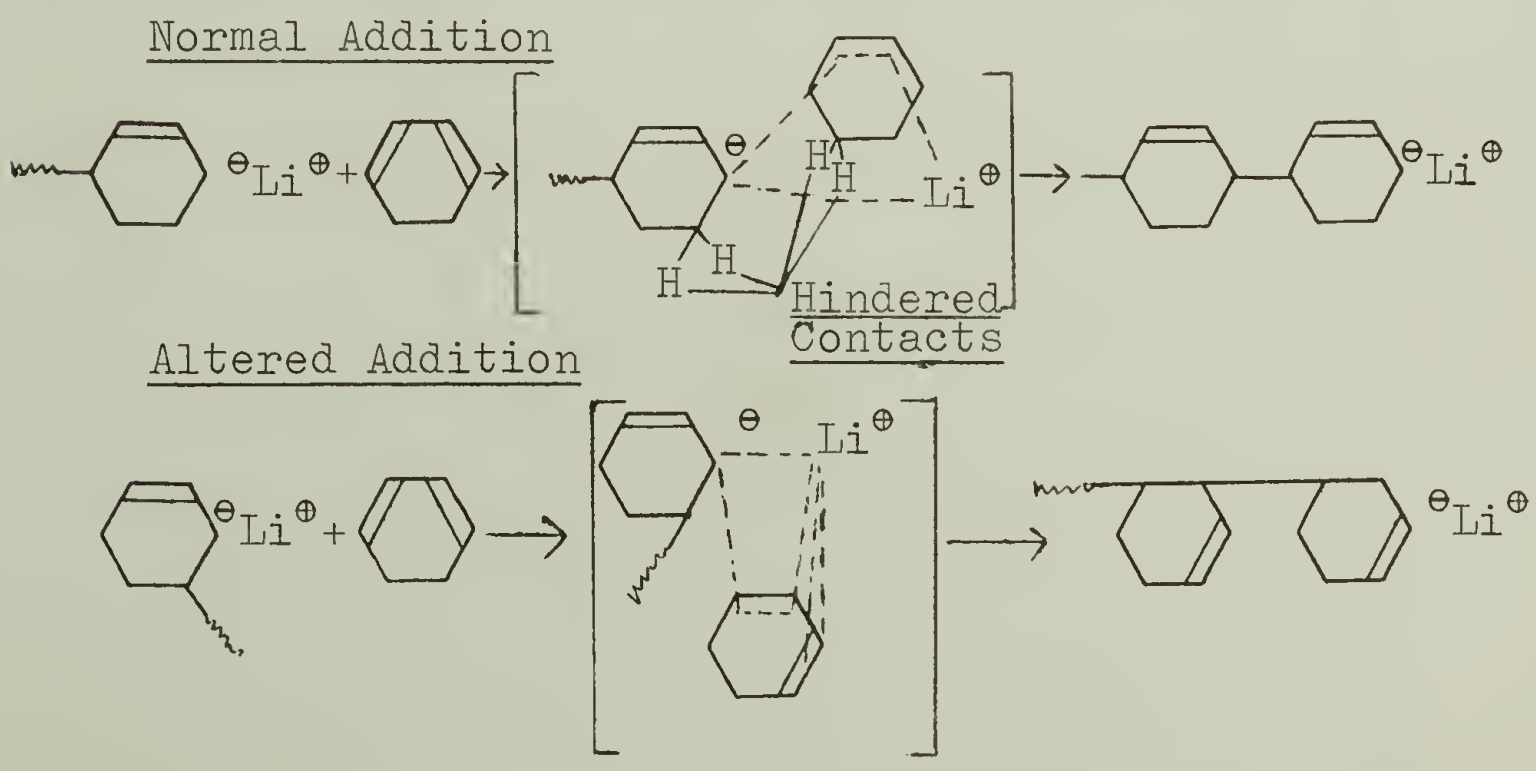
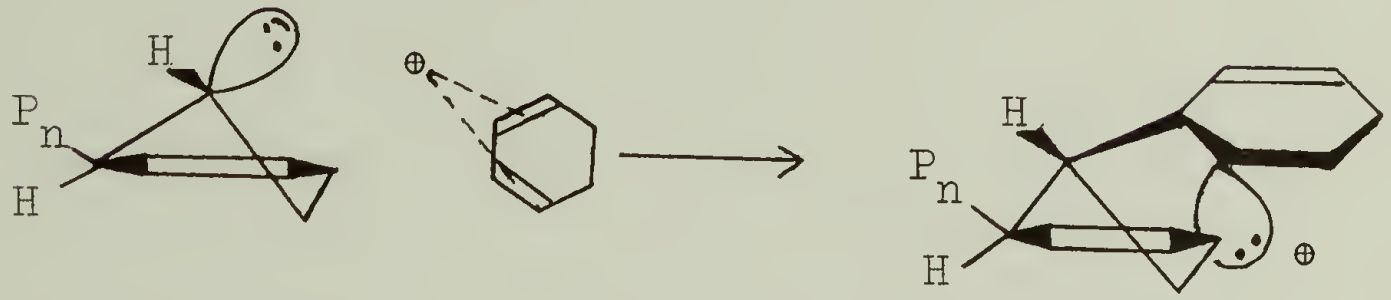


Figure D 9. cis vs. trans Ring Placement in Polycyclohexadiene Polymerization.

A. Non-Solvating (tight ion pair) Media.



I. Carbanion and counterion are "above" plane of the terminal ring before addition.

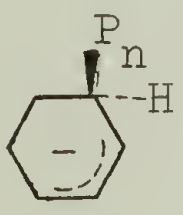
II. After addition, carbanion and counterion are below the plane of the terminal ring unit.

Side View of Chain:

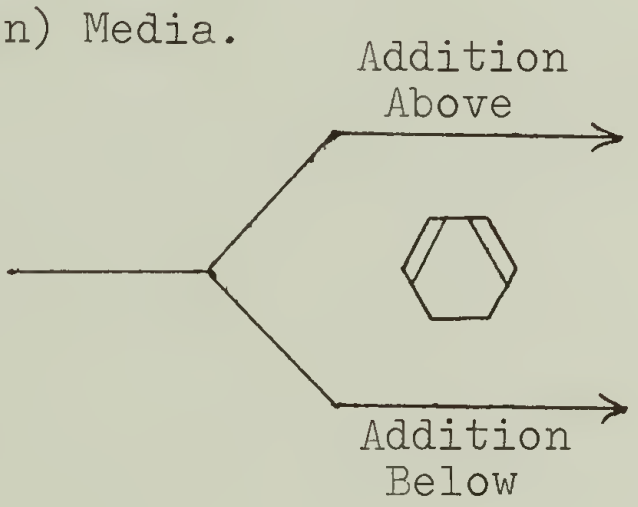
= ring repeating units

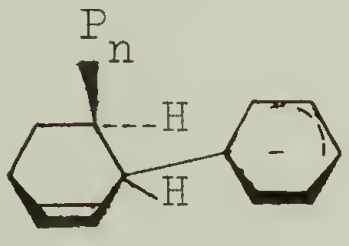
III

B. Solvating (free ion) Media.



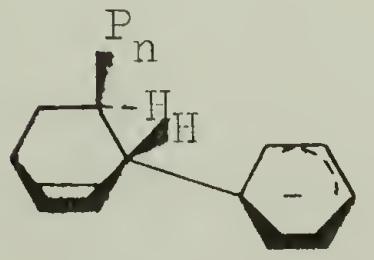
IV





V

cis



VI

trans; favored for steric reasons

dienes, subsequent additions proceed at the C_2 carbon (Figure D8-III) which is a secondary anion and hence the most reactive of the three carbon centers making up the allylic system. In the case of 1,3-CHD, however, secondary anion centers are formed at positions C_2 and C_4 in the derived allylic species. Therefore, further addition could occur from either center. Further, on the basis of steric considerations, 1,4 addition would be slightly more favorable (Figure D8-IV, V). These considerations contradict the infrared interpretations given previously and represent an unresolved discrepency which may have to be reconsidered if further experimental data becomes available on polycyclohexadiene microstructure (i.e., C^{13} nmr).

In regard to ring placement, it is suggested that complexation in non-polar media (9 I) leads to insertion across the plane or face of the incoming monomer ring (9 II) so that eventually adjacent repeating units will be located on the same side of a given repeating unit; this is termed <u>cis</u> addition. Such a mechanism would cause the counterion to occur alternately above and below a plane containing the monomer. This results in a zig-zag arrangement of <u>cis</u> placed repeating units (9 III). In polar media, propagation occurs via the solvated carbanion (9 IV). Presumably, therefore, when the counterion is not

closely attached to the anion, propagation could result in either cis (9 V) or trans (9 VI) ring placement. It is postulated that trans addition (in which the incoming monomer adds on the carbanion face opposite the side possessing the polymer chain) is favored for steric reasons and accounts for the previous nmr results.

E. Polar additives in 1,3-CHD polymerization. The addition of carbon dioxide to the anionic polymerization of 1,3-CHD with n-butyllithium has previously been reported (pp 39-44) to be a possible means of molecular weight enhancement. In our work we have incorporated carbon dioxide in anionic polymerizations of 1,3-CHD in an attempt to produce high molecular weight polycyclohexadiene and we have conducted polymerizations in the presence of various polar additives which might approximate the possible effects of carbon dioxide addition. Polymerizations conducted with the carbon dioxide additive in the present work did not cause any significant improvements in either molecular weight, per cent conversion, or softening point range of the resultant polycyclohexadienes. The results are summarized in Table D7.

As previously discussed, it is possible that addition of carbon dioxide additive produces a complex mixture of $Bu_2C(OLi)_2$, dibutyl ketone and lithium hydroxide (p 42)

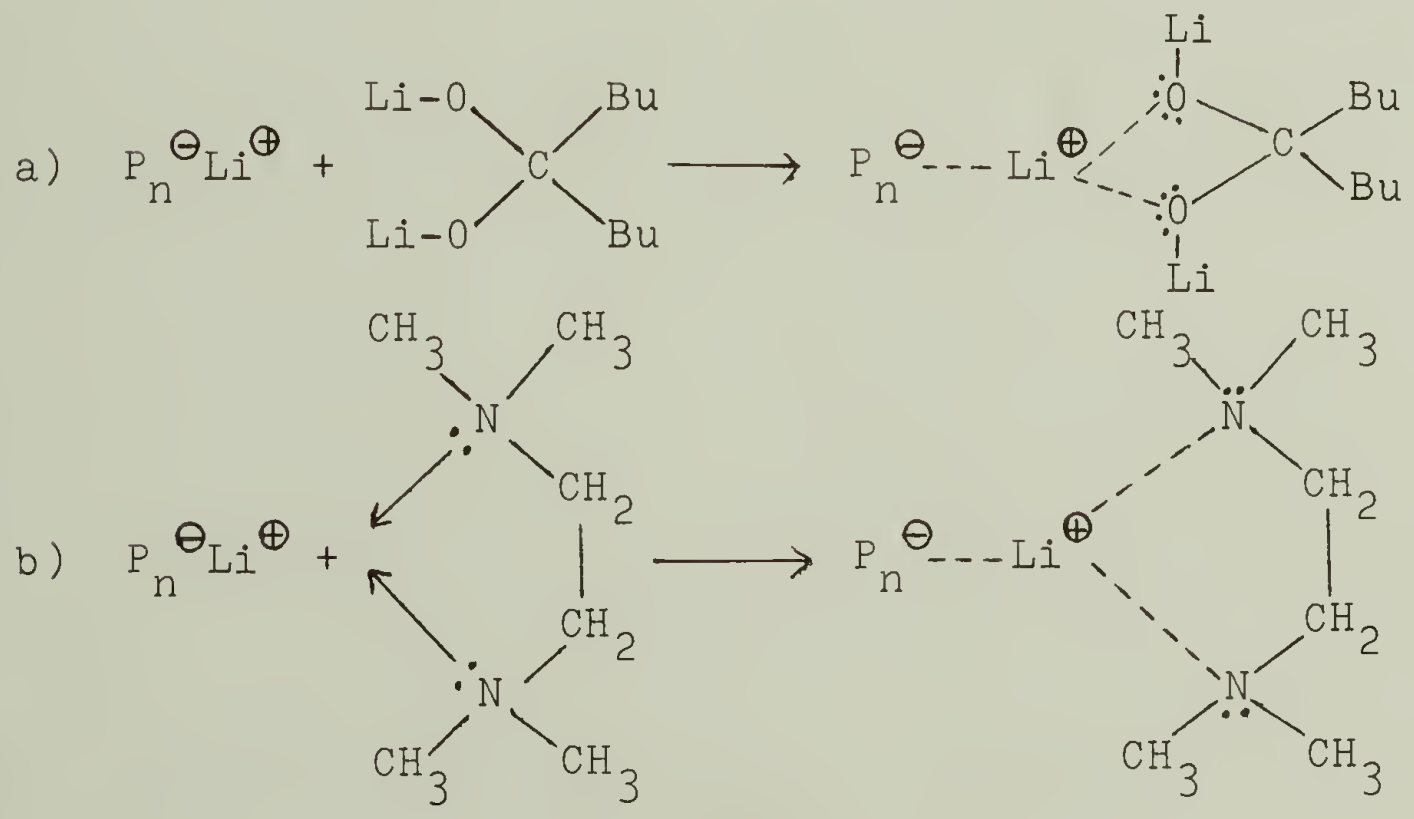
TABLE D7

EFFECT OF POLAR ADDITIVES ON THE ANIONIC POLYMERIZATION OF 1,3-CHD

Sample	Synthetic Cond.	Additive	% Conv.	Sft. Pt. Range	$\overline{Mn}$
P- 50- 1	THF/R.T.	none	. .	101-106	3100
P-102- 1	THF/-78°	none	95.0	x-links before melting	. .
P-102- 3	THF/25°	none	92.5	120-126	3005
P-100- 9	THF/-78°	BuLi/CO_2	97.0	120-124	. .
P-100-10	THF/-78°	BuLi/CO_2	66.0	109-114	. .
P-100-11	$\emptyset CH_3$/-78°	BuLi/CO_2	. .	. .	. .
P-102- 8	THF/-78°	BuLi/CO_2	96.0	132-138	6494
P-102- 9	$\emptyset CH_3$/0°	BuLi/CO_2	. .	. .	. .
P- 76- 2	THF/-78°	TMEDA	. .	. .	. .
P-100-12	$\emptyset CH_3$/-78°	TMEDA	none	. .	. .
P-100-13	n-hexane/-78°	TMEDA	8.0	95-100	. .
P-102- 6	cyclohexane/0°	TMEDA	56.0	x-link before melting	. .
P-119- 1	n-hexane/-78°	TMEDA	trance	132-140	. .

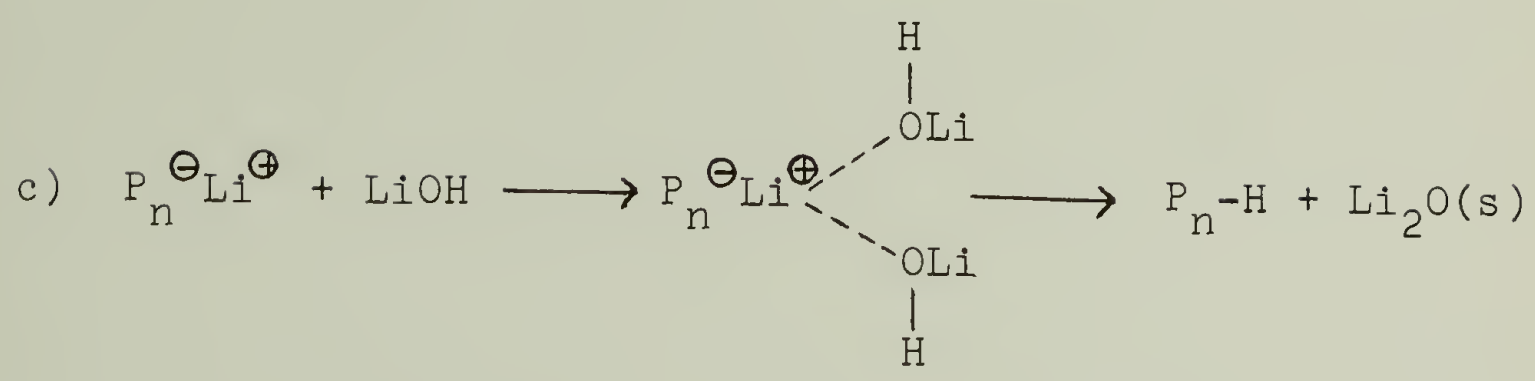
which may have two possible modes of action. The polymerization may be homogeneous with the additives complexing with the carbanion/counterion pair (Figure D10, a). This homogeneous reaction might be approximated by carrying out an anionic polymerization in the presence of TMEDA (a model for $Bu_2C(OLi)_2$ (Figure D10, b), although as noted in Figure D10c,d, lithium hydroxide and dibutyl ketone in themselves are chain termination agents for the polymerization.

FIGURE D10. Theory for the Nature and Function of the Lenz-Adrian BuLi-CO_2 Catalyst.

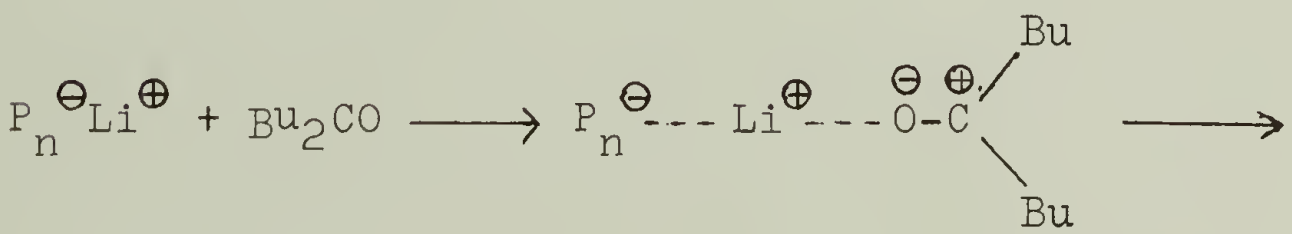


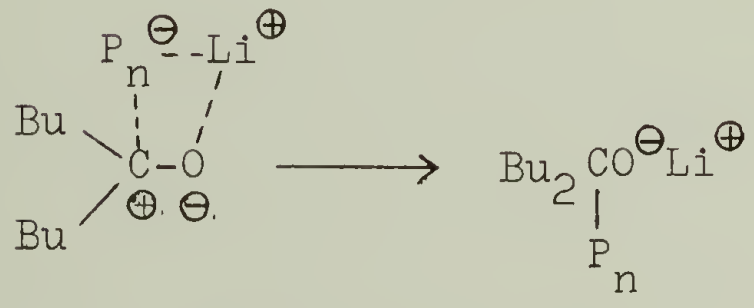
TMEDA/Li complex increases the rate and molecular weight in the anionic polymerization of ethylene (46).

FIGURE D10--Continued

c) 

Lithium hydroxide is known to react with polymeric carbanions to form lithium oxide and, hence, is a chain terminating species (41).

d) 



Dibutyl ketone can react with the polymeric carbanion to form a Li alkoxide and would also be a chain terminating agent.

Alternatively, the ionic materials just referred to may form a surface on which a heterogeneous reaction could ensue. This situation is superficially similar to the Alfin catalyst system (79), which to date has not been

utilized for this monomer. The Alfin system is composed of a metal alkyl (e.g., alkylsodium), an alkali halide (e.g., sodium chloride), and an alkali metal alkoxide (sodium isopropoxide) which form a complex surface onto which the monomer is presumably adsorbed and activated by complexation at an active site (100-104). The work reported here was conducted in a soda bottle applied by the catalyst manufacturer. The bottle contained 250 ml of dried pentane which, it has since been ascertained was saturated with 1,3-butadiene gas. In retrospect, it is possible that the material referred to below is really a mixed trans-1,4- and 1,2-polybutadiene.

The effect of adding TMEDA is summarized in Table D7 and indicates no significant enhancement in molecular weight, conversion or softening point range. In the Alfin polymerization a 68% yield of a completely toluene-soluble, white, strong rubber-like material was formed in contrast to the white powder which results from anionic polymerization. The polymer is apparently of high molecular weight although this property was not determined.

The infrared spectrum of the product (IR 1) is peculiar compared to the spectrum normally obtained for polycyclohexadiene (IR 17). The principle peaks and their assignments are summarized and compared in Table D8 for the

TABLE D8

COMPARISON OF THE INFRARED SPECTRA OF ALFIN AND ANIONICALLY POLYMERIZED 1,3-CYCLOHEXADIENE

Anionic (THF/BuLi)	Alfin	Band Assignment
	3080	asym. olefin C-H str. (terminal olefin)
	3030	olefin C-H str. (<u>trans</u> olefin)
3015		olefin C-H str. (<u>cis</u> olefin)
	2990	symm. olefin C-H str. (terminal olefin)
1680		C=C stretch
1650		C=C stretch
	1672	C=C stretch for CHR = CH_2
	1640	C=C stretch for CHR = CHR
	995 912	C-H olefin deformation for $RCH=CH_2$; both bands required for assignment
	968	C-H olefin deformation; <u>trans</u> olefin
765		C-H olefin deformation; <u>cis</u> olefin
720		C-H olefin deformation; <u>cis</u> olefin

Alfin polymer and an anionically polymerized polycyclohexadiene. The assignments are based on guidelines given by Belamy (94). In the Alfin product, the residual unsaturation occurs as trans and terminal vinyl ($RCH=CH_2$) groups. Such structures could only arise from opening of the diene ring during polymerization which, if true, is heretofore unknown for a cyclodiene system. This work must be repeated using separately prepared pentane solutions and further characterization carried out to understand and verify these results.

III. Hydrogenation of Polymeric Substrates with Diimide

A. Introduction. Hydrogenation of polycyclohexadiene to polycyclohexane with diimide was initially of interest in determining the structure of the precursor polymer. The technique exhibited a number of favorable synthetic characteristics and the final aim of this thesis was to evaluate the generality and characteristics of this reagent in its reaction with high molecular weight substrates. Polymers investigated included polybutadiene homo- and copolymers, polycyclohexadiene, polyisoprene, poly(2,5-dimethyl-2,4-hexadiene), poly(2,3 dimethyl-1,3-butadiene) and poly(2-chloro 1,3-butadiene). These materials

illustrate the effects of structural changes at or near the residual polymer double bond on the utility and generality of the reaction with polymers.

B. General procedure and comments. For application of the technique to polymers diimide was generated by the unimolecular decomposition of p-toluenesulfonylhydrazide, p-TSH, which allowed mutual solubility of the polymer, product and hydrogenation agent at all degrees of conversion when the reaction was conducted in aromatic media (see p 121 and solubility chart, p 124). This feature of common solubility is thought to be critical. For example, polycyclohexadiene was 45% hydrogenated when a 50/50 diglyme/toluene mixture, in which neither starting polymer nor product were soluble, was used as the solvent. In toluene only, polycyclohexadiene is soluble but the product polycyclohexane is not, and the observed conversion was 80% under otherwise similar conditions. Finally, complete hydrogenation occurred in both xylene and mesitylene which are solvents for all components of this system.

For reaction, a 3% weight to volume solution of the polymer dissolved in mesitylene, xylene or toluene was allowed to react at a 2/1 mole ratio of p-TSH/olefin under a nitrogen blanket, at reflux, for four hours. The p-TSH dissolved at 75-90°C. The aromatic solvent used in a given

case was dependent upon ease of product workup. It was most desirable to use the lowest boiling solvent consistent with dissolving all components of the reaction system. For example, in the reaction of polycyclohexadiene the product precipitated easily from xylene, but mesitylene gave a chalk-like suspension which was difficult to isolate (see p 121).

C. Empirical verification of diimide hydrogenation of polymeric substrates. The conversion of unsaturated precursor polymers to partially or completely hydrogenated derived polymers was verified by infrared spectroscopy and elemental analysis, and when sample behavior permitted, by nmr and thermal (DSC and Fisher-Johns softening points) analysis. This section summarizes and comments upon the analytical results obtained for each system examined.

Trans-1,4-polybutadiene. Elemental analysis gave a calculated conversion to polyethylene of 74.3% according to the procedure outlined in Appendix 7.

The infrared spectra of the product indicated complete loss of bands at 3020, 1660, 965, and 910 cm^{-1} present in the spectra of trans-1,4-polybutadiene and related to olefin structure (p 132). Two new bands at 720 and 730 cm^{-1} appeared in the product spectrum and are characteristic of $-CH_2-$ rocking vibrations for the crystalline

and amorphous regions of polyethylene, the anticipated product.

Thermal analysis of the product (p 133, DSC-2) indicated a polyethylene melting transition of 118°C typical for low density polyethylene. Because this initial polymer had a 1.4% vinyl content, complete hydrogenation would produce a polyethylene having approximately 15 branches ($-CH_2CH_3$ branches) per 1000 carbon atoms. Thus, the observed melting point is in good agreement with that expected (83; Table D9) for a branched polyethylene.

TABLE D9

MELTING POINTS OF POLYETHYLENE AS A FUNCTION OF THE NUMBER OF CH_3 GROUPS PER 1000 CARBON ATOMS

No. CH_3/1000C	T_m(°C)
87	105
28	108
28	113
8	123
0	132

Hydrogenated <u>trans</u>-1,4-polybutadiene in this work:

15 ($-CH_2CH_3$)	118°C

Styrene-butadiene copolymers.

Styrene-butadiene-styrene block copolymer. The observed increase of 2.38% in hydrogen (SBS-3, p 134) content corresponds closely to the value of 2.28% calculated for quantitative reduction of a 70/30 SBS copolymer.

Nmr analysis of sample SBS-2 (p 135, NMR-10) which was somewhat less hydrogenated (hydrogen increase by elemental analysis was 2.23%) showed an absence of olefin proton peaks at 5.00 and 5.32 ppm present in the starting material (SBS-1, NMR-9). Concurrent with this loss, a new peak at 1.22 ppm appeared; it was assigned to the methylene protons in isolated $-CH_2-$ sequences. The ratio of the number of vinyl to aliphatic protons in SBS-1 vs. SBS-2 was used to calculate (p 135) a conversion of 92%, in good agreement with the value of 97% calculated from elemental analysis.

Infrared spectra of SBS-2 (IR 20b) and SBS-3 (IR 20c) did not possess the olefin bands at 1640, 1654, and 965 cm^{-1} present in the spectra of the starting material (SBS-1, IR 20a) (p 134). The band at 910 cm^{-1} (vinyl) was considerably reduced but not eliminated. The infrared spectrum of polystyrene (IR 21) suggests that this residual adsorbance is due to the strong polystyrene band at 907 cm^{-1}, rather than residual vinyl unsaturation. It is interesting that the product spectra both exhibit the

doublet band at 720/730 cm^{-1} associated with polyethylene crystallinity. This is consistent with the block nature of the starting material which would result in a long polyethylene sequence after hydrogenation.

The DSC traces of SBS-2 and SBS-3 (DSC-3) exhibited polyethylene-like melting transitions at 70°C and 92°C, respectively. The starting material exhibited no observed transitions in the range 326° to 593°K (Table E19).

Styrene-butadiene random copolymer. The observed increase of 2.48% in hydrogen for the most hydrogenated sample (SBS-R-8) corresponds to 94% of the 2.65% hydrogen increase calculated for quantitative hydrogenation of a random 82% butadiene-18% styrene copolymer.

Nmr spectra of increasingly hydrogenated samples (NMR-16-18) were characterized by gradual loss of vinyl protons at 4.96 and 5.30 ppm with growth of a peak at 1.2 ppm assigned to the methylene sequences arising from hydrogenation.

Infrared bands observed at 1650 cm^{-1}, 965 cm^{-1}, and 910 cm^{-1} in the starting material spectra (SBS-R-1, IR 32h). The band at 720 cm^{-1} due to $-CH_2-$ rocking vibrations of polyethylene, occurred alone; the band at 730 cm^{-1}, apparent in the hydrogenated styrene-butadiene block polymer, was not observed. This result is in accord with the random nature of the copolymer.

Polycyclohexadiene. Quantitative hydrogenation of polycyclohexadiene yielded polycyclohexane, which may be polymerized directly from cyclohexane only by treatment at extreme pressure (84) and only to very low molecular weight. The hydrogenation procedure developed here is thought to be the only known practical route to this polymer. In summary, the hydrogenation to polycyclohexane is apparently complete and crosslinking or degradation of the polymer did not occur. Discussion in this section refers specifically to the conversion of polycyclohexadiene P-50-1 to polycyclohexane P-54-1 (p 121). However, examination of similar samples indicated that these results were typical and reproducable (Tables B,C,D, Appendix 7).

The formation of polycyclohexane is supported by several independent observations. Cyclohexene, a low molecular weight model compound for polycyclohexadiene, was converted in 77% yield (p 79) to cyclohexane by diimide from the thermal decomposition of p-TSH. Bands and peaks characteristic of olefin content in the infrared and nmr spectra of polycyclohexadienes were quantitatively absent after diimide hydrogenation (p 81,83), and bands attributed to saturated content were observed to appear or increase. Thus, the bands at 3015, 1680, 1650, 765, and 720 cm^{-1} in the infrared spectra of polycyclohexadiene (IR 17) were

completely removed upon hydrogenation, while bands at 2920, 2850, and 1460 cm^{-1} (film) increased (IR 18). Similarly, the olefin proton peaks at 5.64 ppm in the nmr spectrum of polycyclohexadiene was lost, while unresolved peaks were found from 0.75 to 2.00 ppm (NMR-1 vs. NMR-8).

Elemental analysis supports this spectroscopic evidence. A hydrogen increase of 1.74% of the total weight was observed and is 80% of the 2.19% increase calculated for quantitative conversion, but nmr analysis of the starting material (p 100, Table E6) indicated that only 83% of the theoretical olefin content was present in the starting but. Thus, the observed value of 80% was in good agreement with what would be calculated for quantitative conversion of the particular sample under consideration.

Other supporting evidence includes the solubility behavior of the hydrogenated material which is altered in a manner consistent with the transformation of a polycyclohexadiene to polycyclohexane. Polycyclohexadiene was soluble in tetrahydrofuran before treatment but insoluble afterwards while polycyclohexadiene is not soluble in cyclohexane, but the hydrogenated product went into solution readily.

Finally, thermal transition points for polycyclohexadiene were shifted significantly after diimide

hydrogenation which can be taken as indirect evidence for a change in polymer structure. Thus, the Fisher-John's softening point changed from 101-106°C before hydrogenation, to 192-195°C after reaction. Also, the DSC thermogram indicated that the transition at 88°C before reduction was raised to 187°C afterwards for the sample studied.

Cis-1,4-polyisoprene. Elemental analysis indicated an increase of 2.18% in hydrogen by weight which corresponds to 94% of the 2.36% increase which would theoretically occur for quantitative conversion.

Bands at 3050, 1680, and 835 cm^{-1} present in the infrared spectrum of polyisoprene (p 138, IR 22) were not apparent in the spectrum of the hydrogenated material (p 92, IR 23) indicating complete conversion on this basis. The nmr resonance of the olefin protons at 5.04 ppm (NMR-11,12, p 138) in polyisoprene are absent after diimide treatment. The methyl protons appeared as a singlet at 1.64 ppm for the starting material; these become a doublet shifted to 0.77 and 0.98 ppm which is consistent with the addition of a proton to the carbon bonded to the methyl group. Finally, the $-CH_2-$ doublet at 1.95 and 2.00 ppm in the starting material become a multuplet at 1.23 ppm, a value close to the 1.30 ppm previously noted in hydrogenated polybutadienes.

Hydrogenation of polyisoprene should form a 1:1 alternating copolymer of ethylene and propylene, a rubber-like material which would be expected to exhibit a low temperature glass transition between that of polyethylene (148°K) and atactic polypropylene (253°K) (85). In particular, this temperature is predictable from the following relationship which arises from the free volume theory of the glass transition (86):

$$\frac{1}{Tg} = \frac{1}{w_1 + Bw_2} \left[\frac{w_1}{Tg_1} + \frac{w_2}{Tg_2} \right]$$

when Tg = glass transition of the copolymer

Tg_1, Tg_2 = glass transition temperatures of the pure homopolymers making up the copolymer.

w_1, w_2 = weight fractions of the individual copolymers.

B = constant for a particular system and is approximately equal to one.

For the 1:1 ethylene-propylene copolymer $w_1 = 0.6$, $Tg_1 = 253°K$ (polypropylene; atactic) and $w_2 = 0.4$, $Tg_2 = 148°K$ (polyethylene), so $Tg = 197°K$. This calculated value compares well with the observed transition at 212°K (DSC-4) found for the hydrogenated polyisoprene. A scan rate of 20°/min was used which could have resulted in a several degree "overshoot" of the Tg.

Poly-2,3-dimethylbutadiene. The amount of hydrogen uptake observed indicated a conversion of 62.5%. Comparison of the infrared spectra of the starting material and product (IR 24,25) films showed a relative decrease of the bands at 1645 and 1690 cm^{-1}, which are assigned to olefin stretching vibrations.

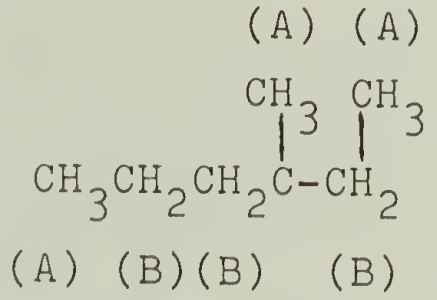
The nmr spectra of the hydrogenated product exhibited broad, overlapping peaks centered at 0.76, 1.20, 1.60 and 1.90 ppm (NMR-13, p 142). The upfield peaks at 0.77 and 1.20 ppm were assigned (see later discussion) to the methyl and methylene protons of hydrogenated repeating units, while those at 1.60 and 1.94 ppm, the downfield set, were assigned to the methyl and methylene protons of non-reduced repeating units. The four peaks were overlapping but existed as two separate groups of two. The areas were estimated by planimeter and, allowing for statistical factors (p 142), the calculated per cent hydrogenation of poly-2,3-dimethyl butadiene was 47%.

Three Sadtler nmr "standard" spectra were available which aided in making the assignments above (Figure D11). The compounds below are structurally similar to the polymer repeating units before (D11-II and D11-III) and after (D11-I) hydrogenation. The methyl protons in I, and those removed from the double bond in II and III have chemical

FIGURE D11. Low Molecular Weight Model Compounds Structurally Related to Poly-2,3-dimethylbutadiene Before and After Reduction.

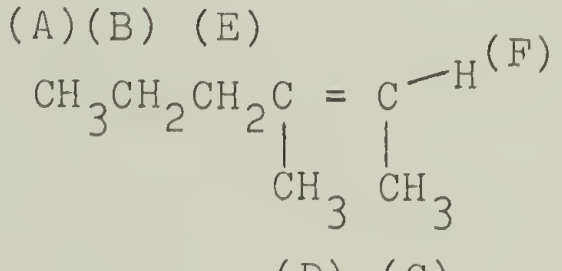
I. Sadtler No. 5312 3-methylhexane

a. 0.89 ppm
b. 1.0-1.6 ppm



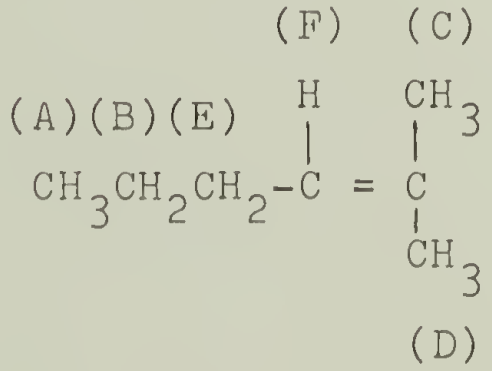
II. Sadtler No. 8005 (cis) 3-methyl-2-hexene

a. 0.89 ppm
b. 1.33 ppm
c. 1.55 ppm
d. 1.59 ppm
e. 1.97 ppm
f. 5.16 ppm



III. Sadtler No. 8004 2-methyl-2-hexene

a. 0.90 ppm
b. 1.29 ppm
c. 1.60 ppm
d. 1.69 ppm
e. 1.95 ppm
f. 5.09 ppm



IVa. Polymer before reduction.

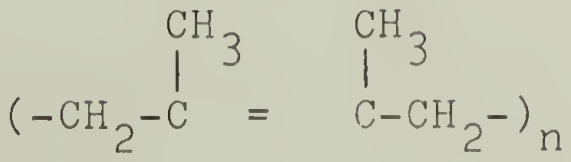
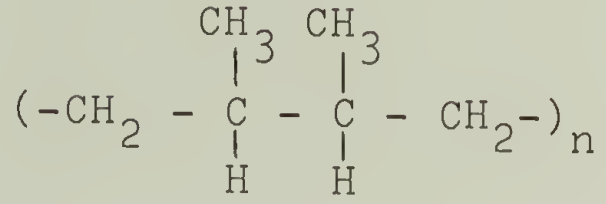


FIGURE D11--Continued

IVb. Polymer after reduction.



shifts of 0.89, 0.89 and 0.90 ppm, respectively. The placement of methyl groups directly on an unsaturated carbon atom (D11-II and D11-III), however, shifts this methyl resonance to 1.55 and 1.59 ppm (D11-II) and 1.60 and 1.69 ppm (D11-III) respectively. This observation suggests assignment of the peaks at 1.60 and 0.76 ppm to the methyl groups of unsaturated (D11-IVa) and saturated (D11-IVb) polymer repeating units. Similarly, the methylene groups next to the double bond in D11-II and D11-III appear at 1.97 and 1.95 ppm respectively, whereas methylene groups next to methyl groups had a proton resonance at 1.33 and 1.29 ppm. The methylene groups in D11-I, which has no unsaturation, appear between 1.0 and 1.6 ppm. Therefore, the methylene resonances at 1.94 ppm in the polymer nmr were assigned to residual unsaturated segments, and those centered at 1.20 ppm to hydrogenated segments.

Poly-2,5-dimethyl-2,4-hexadiene. Comparison of the amount of hydrogen uptake observed by elemental analysis (0.36%) to the amount expected for 100% conversion (1.60%) gave a calculated conversion of 22.5%.

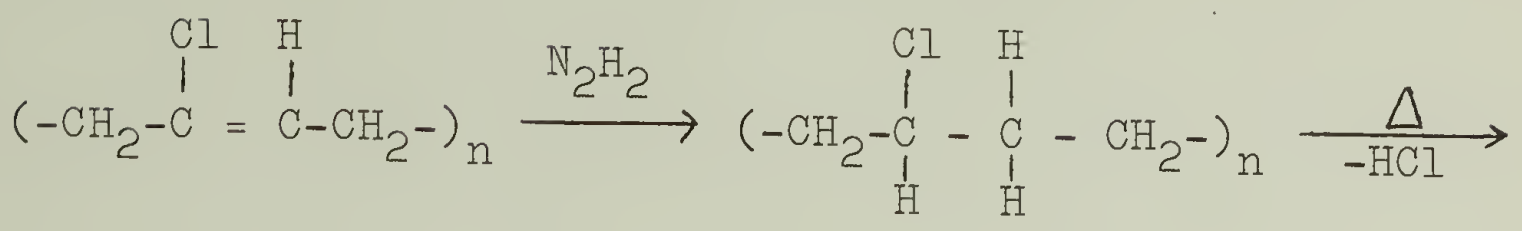
Infrared spectra (IR 26,27) determined on melt cast films indicated a decrease in the relative adsorbance of bands at 3032, 1675, 945 and 815 cm^{-1} which is consistent with the partial hydrogenation observed by elemental analysis.

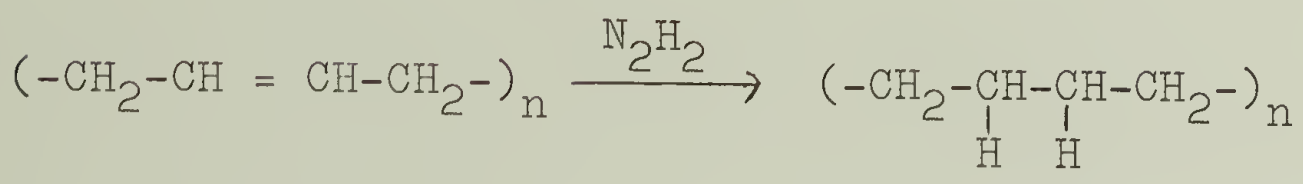
Fisher-John's softening points were determined for samples before and after hydrogenation and a gradual decline in softening point was noted.

	Softening Range (°C)
Starting material	230-240
One 12-hour reduction	210-220
Two 12-hour reductions	190-200

Poly-2-chlorobutadiene. Elemental analysis before and after hydrogenation corrected to 100% C+H+Cl indicated a hydrogen increase of 0.23%, equivalent to 11% reduction. The elemental analysis also indicated a decrease in chlorine content of 1.75%, or 5.25% of the amount of chlorine originally present. This loss suggests partial dehydrohalogenation of the thermally unstable polyvinyl-chloride/polyethylene copolymer which would be formed upon hydrogenation of Neoprene (Figure D12).

FIGURE D12. Loss of Hydrogen Chloride during the Hydrogenation of Neoprene.





D. Effect of altering the polymeric substrate.

The utility of polymer hydrogenation by diimide is affected by the type and degree of substitution occurring at or near the residual double (Table D10). Samples 1 to 5 represent various examples of disubstitution. Sample 4, having 30% vinyl content in the butadiene portion, contains both monosubstitution and disubstitution. The vinyl units also represent a case of pendent group unsaturation. Sample 6, polyisoprene, is trisubstituted while sample 7, methyl rubber, corresponds to a tetrasubstituted olefin double bond. In sample 8, poly-2,5-dimethyl-2,4-hexadiene, the four methyl groups reside on the carbon atoms adjacent to the carbon atoms of the double bonds. Finally, sample 9, poly-2-chlorobutadiene, possesses a polarized bond because of the electron-withdrawing chlorine atom.

In general, polymeric substrates react in a manner predicted by analogous low molecular weight materials.

TABLE D10

PER CENT HYDROGENATION OF POLYMERIC SUBSTRATES AS A FUNCTION OF DOUBLE BOND STRUCTURE

	Polymer	Solvent	Time	p-TSH/ Olefin	% Conversion		
					Elemental	IR	NMR
1.	trans-1,4-polybutadiene	xylene	4.5	2.0	74.4	100	. .
2.	cis-1,4-polybutadiene	toluene	6.0	1.5	81.0	. .	. .
3.	styrene-butadiene-styrene block copolymer	xylene	4.0	2.0	100.0	100	. .
4.	styrene-butadiene-random copolymer	toluene	2.0	2.0	93.5	98	. .
5.	polycyclohexadiene	xylene	5.0	2.2	89.0[a]	97	100
6.	cis-polyisoprene	xylene	4.0	2.0	94.0	100	100
7.	methyl rubber	$\frac{\text{DCH}^c}{\text{xylene}} = \frac{75}{25}$	12.0	2.0	62.5	. .	47[b]
8.	poly-2,5-dimethyl-2,4-hexadiene	$\frac{\text{DCH}^c}{\text{xylene}} = \frac{25}{50}$	4.0	2.0	22.5	. .	. .
9.	poly-2-chlorobutadiene	xylene	4.0	2.0	11.0	. .	. .

[a]Less than theoretical olefin content in starting material.

[b]Spectra were badly overlapped.

[c]DCH = decahydronapthalene.

Polymers which exhibit mono-, di-, and trisubstitution (Table D10-1 to D10-6) are quantitatively hydrogenated by diimide. Further substitution (e.g., D10-7) reduces the effectiveness of diimide reduction to 50%, even after extended treatment to 12 hours to allow for a possibly slower reaction rate. These observations are consistent with the behavior of low molecular weight olefins where an adverse effect upon rate and conversion results from increased substitution on the olefin carbon atoms, caused, apparently, by steric crowding in the transition state.

It was interesting that poly-2,5-dimethyl-2,4-hexadiene was reduced less than methyl rubber. Apparently the methyl groups are still sufficiently close to the reaction center to adversely affect the conversion. Also the inertness of Neoprene to diimide is in good agreement with known inertness of this reagent to polar multiple bonds in low molecular weight compounds (pp 56-58).

The above results are subject to other empirical factors. Both methyl rubber and poly-2,5-dimethyl-2,4-hexadiene are insoluble in xylene so a mixed solvent of 30 to 35% tetralin was required to form a homogeneous system. This media should be less able to support the polar transition states which are involved in diimide generation and reaction with olefins. Also, the

hydrogenation of methyl rubber and poly-2,5-dimethyl-2,4-hexadiene may be obviated because of self-disproportionation (pp 58-59) rather than complete inertness of the substrate to diimide.

E. Molecular weight changes during diimide reduction; the effect of altering the p-TSH/olefin ratio. It has been shown (75, p 73) by Nakagawa et al. that poly(vinyl chloride) treated with p-TSH for four hours at 100°C in chlorobenzene did not undergo crosslinking or degradation. In our present work (Table D11) we have observed similar behavior for polyisoprene and polycyclohexadiene treated with p-TSH in xylene under nitrogen for four hours at reflux (Table D11).

TABLE D11

EFFECT OF DIIMIDE REDUCTION UPON MOLECULAR WEIGHT

Sample	Number Average Molecular Weights		
	Before Reduction	After Reduction	Anticipated
Polycyclohexadiene			
P- 50-1	3,160	3,790	3,240
P-102-8	6,500	9,400	6,660
Polyisoprene	150,000(est.)[a]	122,800	154,400

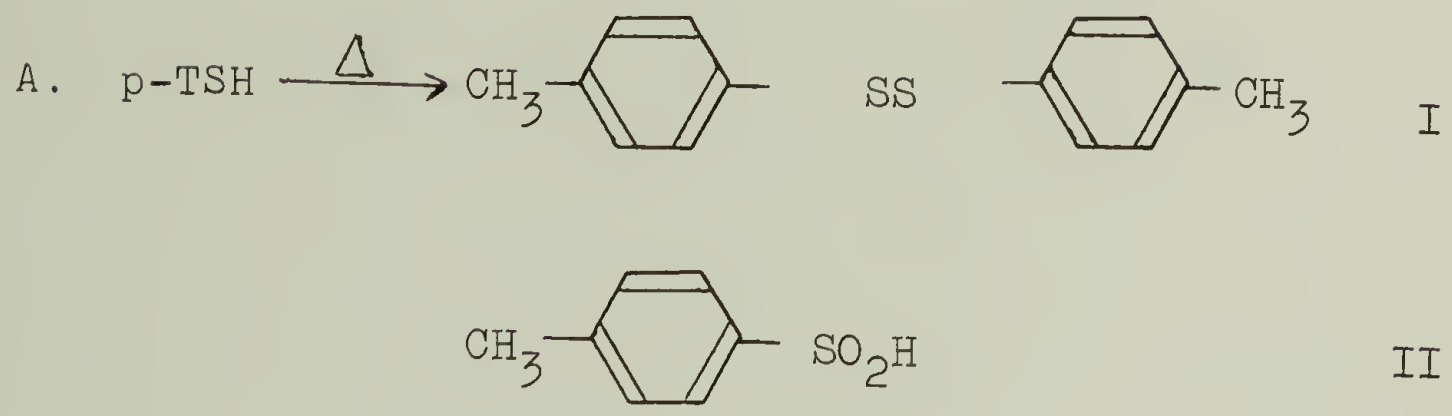
[a]On the basis of previous product results, the manufacturer estimates a $\bar{M}n$ of approximately 150,000; we are presently evaluating this material.

The $\bar{M}n$ of 122,800 found for polyisoprene after hydrogenation seems in good agreement with the approximate value of 150,000 quoted by the manufacturer. The polycyclohexadiene samples exhibited molecular weight increases beyond a level accountable by hydrogenation alone and at present, there is no definite explanation for this.

In one experiment a series of polybutadiene hydrogenations were conducted in xylene, and the ratio of p-TSH/olefin was varied from 0.8 to 2.0 (p 147). When the reactant ratio dropped below 1.5, the system formed a crosslinked gell. This result suggests that residual polymer unsaturation which is not removed, or not removed rapidly enough, may be susceptible to radical or cationic crosslinking. Thus, oxygen should be rigorously excluded from the reaction, and it may be useful to add a mild organic base (e.g., a tertiary amine) to the system as an acid scavenger.

F. Byproduct substitution during diimide reduction. Diimide reduction with p-TSH can lead to side reactions (p 63, Figure D38) which may form products capable of reacting with residual double bonds of the polymeric substrate before the latter is completely reduced (Figure D13). Characterization of the products of this reaction has led to evidence suggesting that substitution of the

FIGURE D13. Side Reaction Products and Their Reaction with Residual Polymer Unsaturation.



sort depicted in Figure D13,c occurs for polybutadiene, and to a lesser extent, for polycyclohexadiene (Table D12).

Reprecipitated cis and trans polybutadienes were found to have approximately 99% hydrocarbon content before reduction with p-TSH. Hydrogenation in xylene at a

TABLE D12

EFFECT OF DIIMIDE REDUCTION ON THE HYDROCARBON CONTENT OF POLYBUTADIENES

	%C	%H	%C+H
A. Solvent toluene; p-TSH/olefin = 1.5/1 (Appendix 7, Table E)			
hi-*cis* polybutadiene			
reaction time = 0 hours	88.02	10.74	98.76
4 hours	81.42	12.81	94.23
hi-*trans* polybutadiene			
reaction time = 0 hours	88.03	10.96	98.99
4 hours[a]	82.53	13.05	95.58
B. Solvent xylene; p-TSH/olefin = 1.5/1 and 2.0/1 (p 85,100)			
hi-*cis* polybutadiene--4 hours reaction time			
ratio = 1.5/1	80.91	13.43	94.34
ratio = 2.0/1	83.77	13.54	97.13
starting material	88.02	10.74	98.76
hi-*trans* polybutadiene--2.0/1.0 = p-TSH/olefin			
reaction time = 0 hours	88.03	10.96	98.99
reaction time = 4 hours	84.13	12.99	97.12

[a]Complete elemental analysis (%)

%C	82.53	%O	1.00	other	1.28
%H	13.05	%S	.52		

2/1 ratio of p-TSH/olefin resulted in products having 97.13% and 97.12% hydrocarbon content respectively. When the p-TSH/olefin ratio was decreased further to 1.5/1, the hydrocarbon content of the product (cis polybutadiene starting material) decreased to 94.3%. Reproducible behavior was noted when toluene was the solvent (Table D12,a), suggesting that the ratio of reactants was related to the lowering of hydrocarbon content. Apparently, non-hydrocarbon materials were chemically incorporated into the products during hydrogenation, and the situation was most pronounced at lower p-TSH/olefin ratios where the unsaturation was removed less rapidly and completely from the system. Further, the amount of non-hydrocarbon materials incorporated within a given system increased with reaction time (Table D13).

These observations are consistent with side reactions, such as those in Figure D13, occurring concurrently with diimide reduction at a slower rate. Confirmation of this possibility was provided by the positive sulfur analysis (0.52%) in the hydrogenated polybutadiene sample (Table D12,a) tested for this element. Assuming the sulfur was present as p-$CH_3ØSO_2$- pendant groups only (later discussion), the 0.52%S requires that one olefin bond in every 90 to 100 originally present in polybutadiene entered into the side reaction proposed in Figure D13,b.

TABLE D13

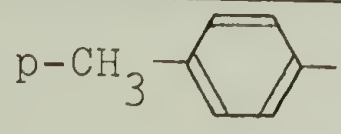
PER CENT OF NON-HYDROCARBON CONTENT IN PARTIALLY REDUCED TRANS-POLYBUTADIENE AS A FUNCTION OF REACTION TIME (APPENDIX 7, TABLE E)

Sample	Reaction Time (hour)	% Non C,H Materials
Ht-1	0.5	1.01
2	0.75	2.47
3	1.0	3.19
4	1.5	3.22
5	2.0	3.43
6	3.0	4.42
7	4.0	4.72
8	6.0	4.43

An ultraviolet spectroscopic investigation was performed using the polycyclohexadiene system. Structurally homogeneous polycyclohexadiene and polycyclohexane do not possess conjugated unsaturation and are not expected to adsorb above 2100 Å in the ultraviolet. However, the phenyl sulfide and phenyl sulfone chromaphores which potentially occur in the hydrogenated product polymer, do adsorb strongly as is summarized in Table D14. The relative extinction coefficients are such that phenyl sulfide would adsorb strongly ($A \geq 1$) near 2550 Å while the phenyl sulfone would adsorb strongly ($A \geq 1$) near 2250 Å if these groups were present in concentrations of 5×10^{-6} molar

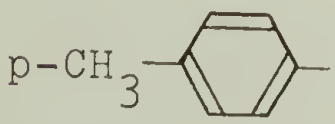
TABLE D14

ULTRAVIOLET ADSORBANCE PROPERTIES OF PHENYL SULFIDE AND PHENYL SULFONE CHROMOPHARES

A.  (Sadtler No. 5638 UV Spectra)

MeOH Solvent 1 cm cell molecular weight=170.23

major peak	A	B	C	D
g/l	0.2	0.2	0.2	0.01
λm (Mu)	272.0	266.5	261.0	224.0
A	0.595	0.640	0.680	0.745

B.  (Sadtler No. 451 UV Spectra)

MeOH Solvent 1 cm cell molecular weight=186.23

major peak	A	B	C	D
g/l	0.2088	0.2088	0.2088	0.0104
λm (Mu)	273.0	267.0	261.0	225.0
A	0.59	0.63	0.61	0.67

C. ØSCH_3 (Sadtler No. 120 UV Spectra)

MeOH Solvent 1 cm cell molecular weight=124.19

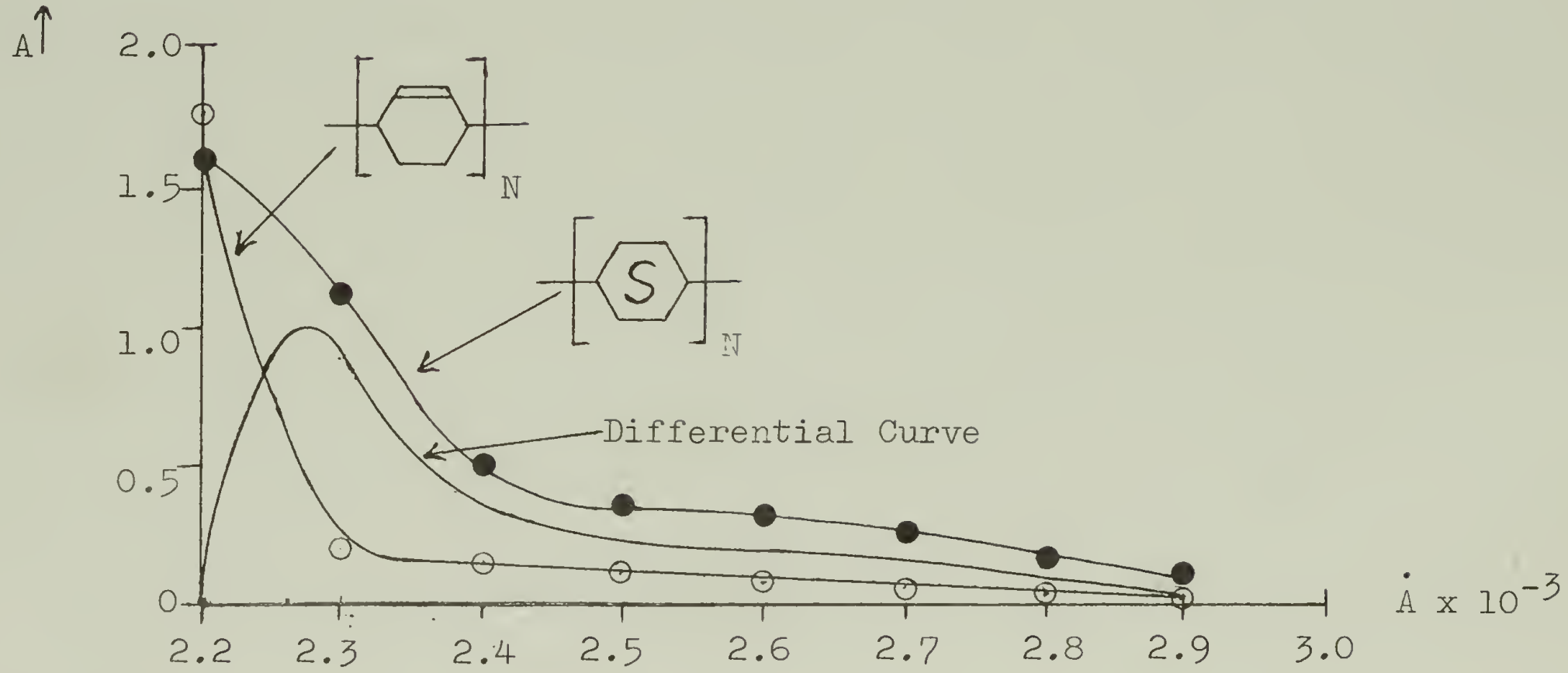
major peak	A	B
g/l	0.0089	0.0089
λm (Mu)	253.0	206.0
A	0.72	0.935

(using 1 cm cell) or greater.

The ultraviolet spectra of polycyclohexadiene and polycyclohexane were determined in an attempt to observe these chromophores. The resulting curves are redrawn in Figure D14; the spectra of the product exhibited a distinct shoulder between 2200 and 2300 Å. Plotting a differential curve (using the curve for the polycyclohexadiene as a "baseline") indicated this shoulder is formed by contributions from a material (s) having its adsorbance maximum around 2275 Å. This is consistent with and supports the postulation that the chromophore involved was $pCH_3ØSO_2-$.

The calculated extinction coefficient, ϵ, at 2250 Å for this substituent is 1.27×10^4 based upon the data in Table D14-a. The adsorbance maximum (at 2.275 Å) in the differential curve in Figure D14 is 1.0. These values yield a calculated chromophore concentration of 7.88×10^{-5} M. Because the concentration of polycyclohexane <u>mer</u> units was 3.56×10^{-2} M, about 1/450 of the double bonds originally present in polycyclohexadiene underwent this reaction at a p-TSH/olefin ratio of 2/1. This result compares to the calculated value of 1/100 determined for polybutadiene at a p-TSH/olefin ratio of 1.5/1, a condition expected to increase the amount of

Figure D 14. Ultraviolet Adsorbance Properties of Polycyclohexadiene before and after Hydrogenation.



Concentrations:

Polycyclohexadiene	0.038 M in THF	Scan Rate 2 1/2 Å/second
Polycyclohexane	0.036 M in cyclohexane	1 cm Path Length

byproduct substitution.

The level of ~1/450 is consistent with the nmr and elemental analysis of polycyclohexane where aromatic protons and sulfur were not detected. At this calculated level, the benzene protons approach 0.1% and the sulfur content would be approximately 0.1%; both figures are below the limits of detection of nmr and elemental analysis, respectively.

G. Relative rates of cis, trans and vinyl reduction in diimide hydrogenation of polybutadiene. The possibility of kinetic selectivity of diimide toward the cis, trans and vinyl groups present in polybutadiene was considered in a semiquantitative fashion by evaluating the per cent conversion vs. time for various polybutadiene substrates. This approach was used for two empirical reasons. Since diimide is the active species rather than the added precursor (p-TSH) there is no direct knowledge of diimide concentration based on the amount of added hydrazide. Also, diimide is a gaseous, transient intermediate (see p 47) so there are no facile means for monitoring its concentration, and a separate study on the decomposition kinetics of p-TSH in toluene and xylene would have been required. Another complication is diimide disproportionation, which occurs at rates comparable to its

reaction with olefins (pp 58-62). The former reaction leads to hydrazine, so the rate of this reaction could have been treated by analyzing and correcting for the amounts of hydrazine formed; however, this determination was beyond the scope of present interests.

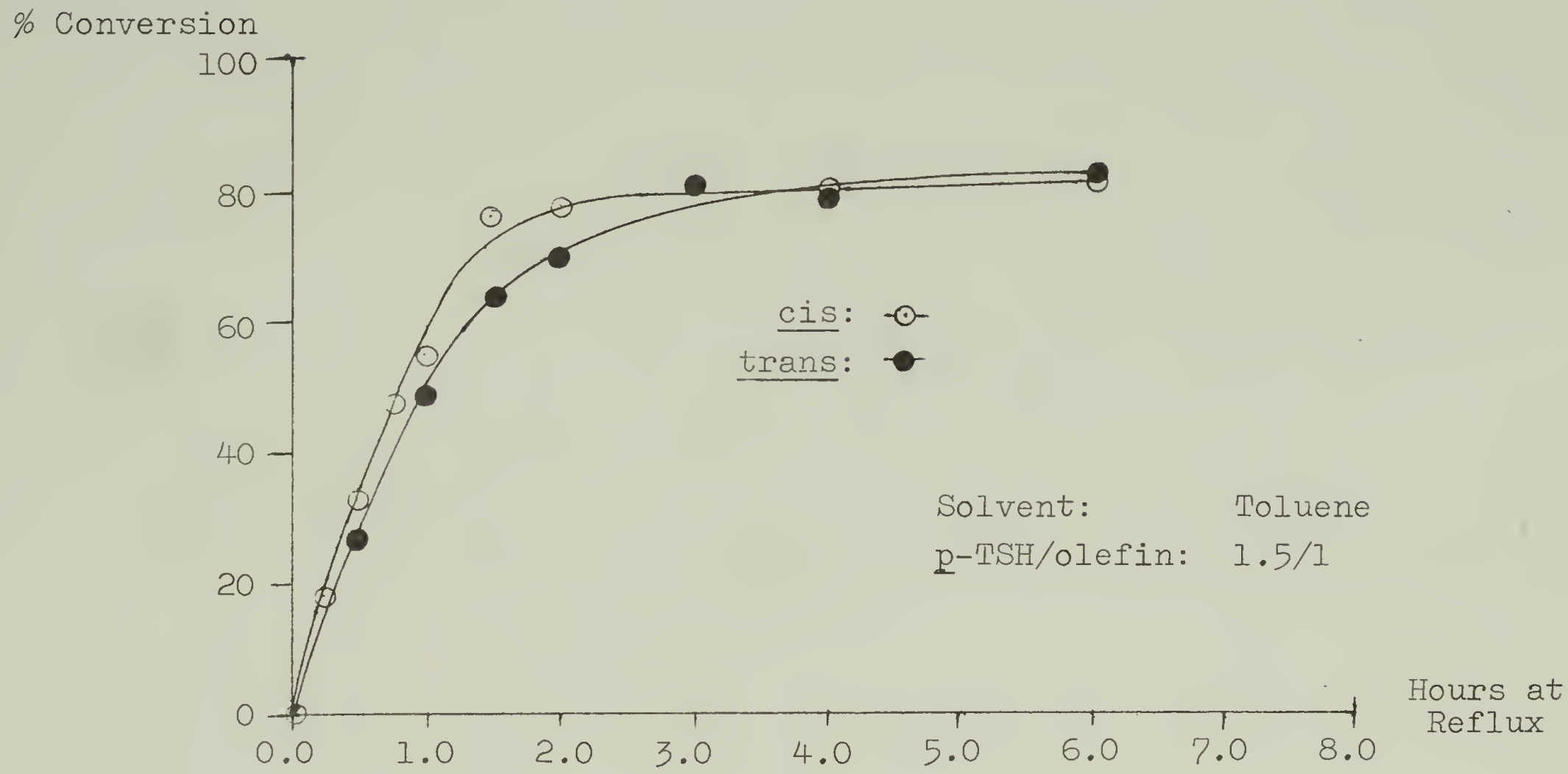
The relative rate of *cis* vs. *trans* hydrogenation was determined by evaluating the per cent conversion *vs.* time of a 93% *cis* (6% *trans*, 1% vinyl) polybutadiene and a 92% *trans* (6.6% *cis*, 1.4% vinyl) polybutadiene treated at a 1.5/1 ratio of p-TSH/olefin in toluene at reflux under nitrogen (p 148). Toluene was specifically chosen because it was the lowest boiling solvent in which the hydrogenation would successfully occur. Under these conditions, any difference in the *cis vs. trans* hydrogenation rates should be maximized. The resulting per cent conversions *vs.* time are given as curves in Figure D15.

Elemental analysis was used to calculate the per cent conversion as a function of time for the partially hydrogenated samples using the relation

$$\% \; U = \frac{2fc-fh}{0.2} \times 100$$

where fc and fh = mole fractions of carbon and hydrogen respectively in the product polymer and fc + fr ≡ 1. Since this method depends basically upon the carbon-hydrogen ratio it is not affected by varying degrees of oxidation

Figure D 15. Relative Rate of Hydrogenation of cis and trans Polybutadiene with p-toluenesulfonylhydrazide.



among the samples and is moderately insensitive to byproduct substitution reactions at the level this was thought to occur. Thus, at 100% conversion, if one assumes that one p $CH_3ØSO_2$- group became substituted for every 50 butadiene repeating units originally present, the calculated conversion would vary by about 5%.

without $pCH_3ØSO_2$- :

$$fc = 0.333$$
$$fh = 0.667$$
$$\% U = \frac{2fc-fh}{0.2} \times 100\%$$

with one p $CH_3ØSO_2$- per 50 butadiene units

$$fc \quad 0.337$$
$$fh \quad 0.663$$
$$\% U = \frac{2fc-fh}{0.2} \times 100\% = 5.5\%$$

To estimate the relative rates of *trans* vs. vinyl reduction, a styrene-butadiene random copolymer containing 70.5% *trans* and 29.5% vinyl butadiene segments was hydrogenated in toluene at a 2/1 ratio of p-TSH/olefin (p 151). The overall per cent hydrogenation (*trans* and vinyl) was determined by nmr analysis and the *trans* vs. vinyl content of the partially reduced samples was found by infrared analysis (Figure D16). Because the original composition was known, it was possible to calculate (Table F, Appendix 7) the relative per cent conversion vs. time for each component separately (Figure D17).

Figure D15 indicates the rate of *cis* and *trans* hydrogenation are equal within experimental error for

Figure D 16. Relative 1,2 vs. 1,4 Content of Partially Hydrogenated Styrene-Butadiene Copolymer.

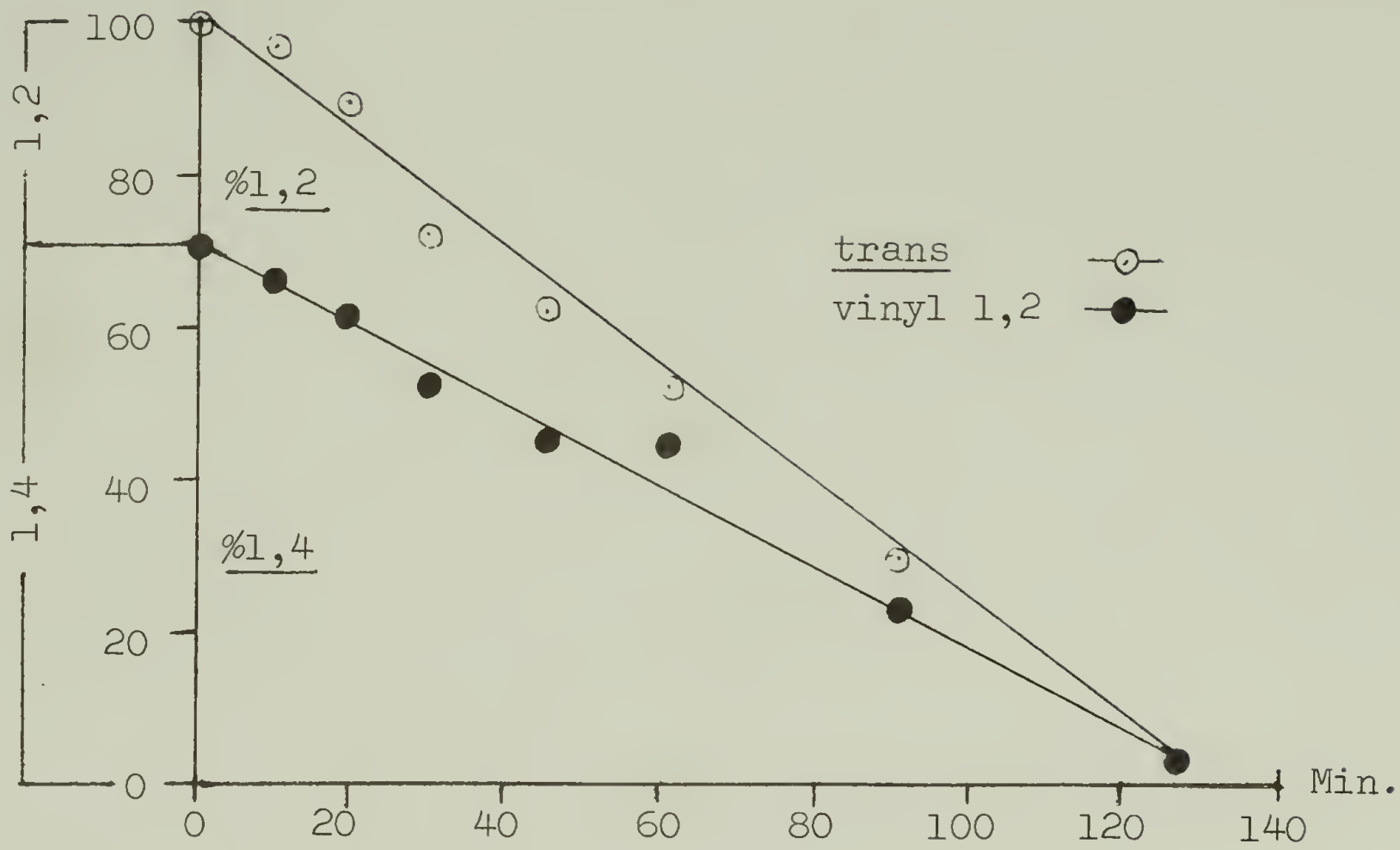
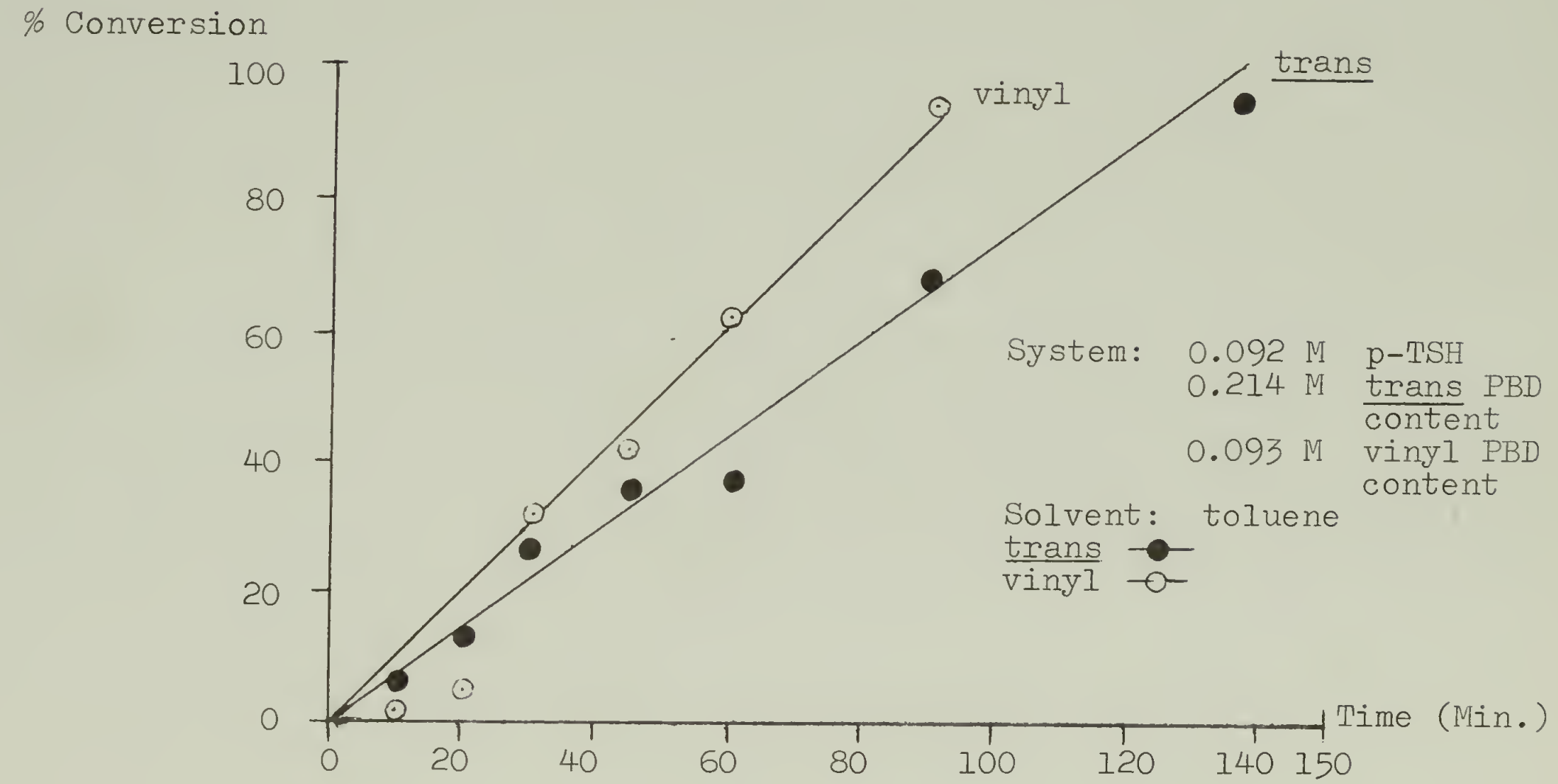


Figure D 17. Relative Rate of Reduction of trans vs. vinyl Content of Styrene-Butadiene Copolymer.



the conditions chosen. This result is expected to hold true for solvents such as xylene and mesitylene which are higher boiling and less kinetically selective. Figures D16, D17 indicate that vinyl 1,2 segments are hydrogenated at a greater rate (e.g., at one and one-half hours around 90% of the vinyl structures were hydrogenated while only 65% of the trans groups had been converted) than the trans 1,4 units. Thus for polybutadiene with diimide at 110°C:

$$k_{cis} \simeq k_{trans} < k_{vinyl}.$$

The more rapid reaction rate observed for the vinyl groups is in accord with this moiety containing the least amount of substitution about the olefin bond, and occurring in a pendent position and hence being more accessible to the diimide reagent.

On the basis of relative rate data determined for a variety of unsaturated acids in previous work (see Table R8, p 52), it was anticipated that k_{trans} would be greater than k_{cis}, as opposed to the observed approximate equality. The study was performed in aqueous media at 25°C. Thus, the elevated temperatures (110-140°C) required in the present work may be above the level where selectivity is sufficiently pronounced to be observed.

H. Thermal behavior of partially hydrogenated polybutadiene homo- and copolymers. DSC traces (Table E19)

of partially hydrogenated cis and trans polybutadiene (DSC-5,6) have been determined as a function of per cent conversion. The first polyethylene-like melting transitions were observed at approximately 60% conversion (Tm=41.8°C at 5°/min) for cis polybutadiene and about 65% conversion (Tm=65.0°C at 5°/min) for trans polybutadiene. As per cent conversion increased the thermogram peaks shifted to higher temperatures and exhibited increasing normalized areas which is indicative of the increased polyethylene content occurring at higher conversions.

When the normalized peak areas are plotted vs. per cent conversion (Figure D18), both sets of curves begin to converge rapidly at higher conversions (80%) which may be expected since both materials give the same final product: polyethylene having 10-15 short chain branches per 1000 carbon atoms. However, over the range of 55 to 80% conversion the DSC peaks for the partially hydrogenated trans polybutadiene exhibited significantly higher melting points and normalized areas at a given degree of conversion.

This behavior is consistent with the first order thermal transition at 75°C for trans-1,4-polybutadiene (Table D15) which makes an endothermic contribution to the DSC thermograms in the temperature range measured in Figure D18. This contribution would be a function of

Figure D 18. Normalized DSC Melting Peak Areas for Partially Reduced Polybutadienes as a Function of Per Cent Conversion.

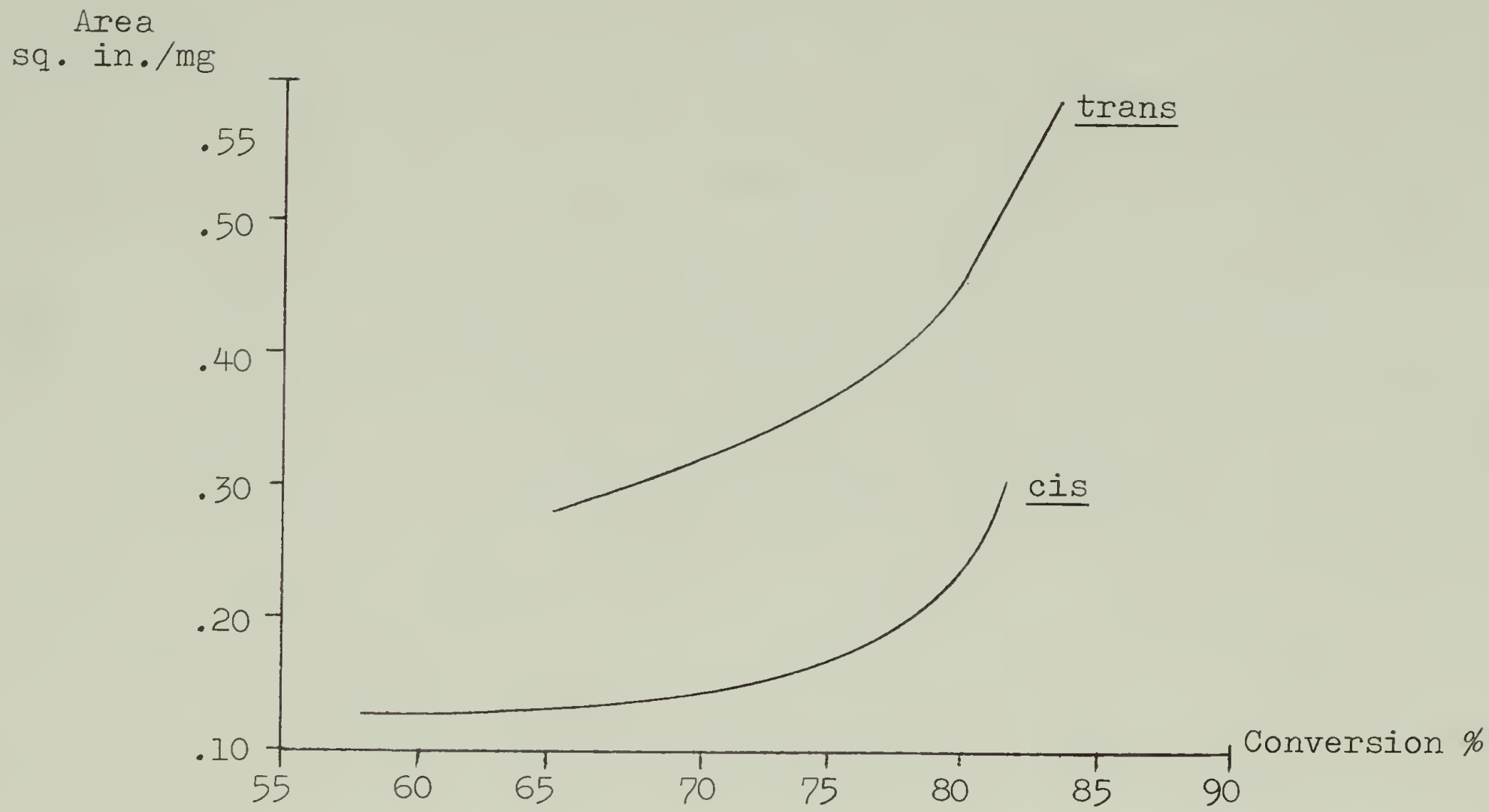


TABLE D15

NATURE OF THE FIRST ORDER THERMAL TRANSITION
AT 75°C FOR TRANS-1,4-POLYBUTADIENE
(85, p 53, section VI)

Modification I $\xrightarrow[75°C]{\Delta}$ Modification II

Lattice for 99% 1,4-trans-polybutadiene: pseudohexagonal; 1 monomer per unit cell

Cell Dimensions (Å):

Axis	a	b	c (chain axis)
Modification I	4.54	4.54	4.90
Modification II	4.88	4.88	4.68

Thermal and Density Parameters:

	Modification I	Modification II
Density (g/cc)	0.93	0.97
Entropy of Fusion (eu/monomer unit $°K^{-1}$)	6.4	2.7
Heat of Fusion (cal/monomer unit)	2400±1000	1100

residual polybutadiene content so the curves in Figure D18 should, and do, converge at higher conversions.

CONCLUSIONS AND RECOMMENDATIONS

I. Conclusions

A. Stereochemistry and mechanism in the anionic polymerization of 1,3-CHD. Molecular weight limitation in the anionic polymerization of 1,3-CHD has been attributed here to degradative chain transfer to monomer. The propagating polymeric carbanion, acting as a strong base, abstracts allylic protons from the monomer to terminate the growing chain and produce a cyclohexadienyl carbanion. This carbanion then eliminates lithium hydride unimolecularly and aromatizes, thus completing a sequence of reactions which limits both molecular weight and conversion.

The diene center in 1,3-CHD, occurring within a six-member ring, was found to exert a significant and characteristic influence upon the architecture of the resulting polymer chain. Polymerization in non-polar media gave predominantly cis placement of adjoining rings in the polymer chain backbone and predominantly 1,2-addition in contrast to the 1,4- type of addition which normally occurs for open chain dienes in such media. Polymerization in solvating media gave predominantly trans rings placement with conventional 1,2- addition of the diene.

B. Hydrogenation of polymers with diimide.

Polycyclohexadiene was quantatively hydrogenated with diimide to polycyclohexane. The nmr spectra of this polymer was useful in characterizing the structure of the precursor polycyclohexadiene. Diimide hydrogenation had previously been utilized only with low molecular weight compounds. It has several features which make its use for the hydrogenation of unsaturated polydienes attractive. Suitable polymers may be efficiently hydrogenated by treatment with p-toluenesulfonylhydrazides, a diimide source, at a p-TSH-to-olefin ratio of 2.0 in aromatic media under nitrogen at reflux for two to four hours. Homopolymers of butadiene, polycyclohexadiene and polyisoprene and styrene-butadiene copolymers may be quantitatively hydrogenated, but alkyl branching at or near the double bonds in the repeating units of the polymer, as in methyl rubber and poly-2,5-dimethyl-2,4-hexadiene, gave conversions less than 50%. Polychloroprene was not hydrogenated by diimide in agreement with the behavior previously noted for low molecular weight olefins (6,12).

Generation of diimide from p-TSH yields byproducts which were also observed to react with the double bonds in polymers undergoing hydrogenation. Thus, between 1/25 and 1/100 of the double bonds originally present in polybutadiene, and 1/500 of the double bonds originally

present in polycyclohexadiene became substituted with p-$CH_3ØSO_2$- groups when the polymers were hydrogenated at 1.5 and 2.0/1.0 p-TSH-to-olefin ratios, respectively, in xylene at reflux. It was also concluded that the p-$CH_3ØSO_2H$ byproduct could be a potential crosslinking agent when the p-TSH to olefin ratio was less than 1.5.

The complete solubility of the products after hydrogenation indicated that excessive crosslinking did not occur during diimide treatment. Polyisoprene and polycyclohexadiene samples on which molecular weights determinations were made before and after hydrogenation also showed no excessive chain scission as a result of hydrogenation.

A limited number of rate studies were preformed to give per cent conversion vs. time data. Under the conditions of toluene reflux and p-TSH-to-olefin ratios of 1.5, the relative rates of hydrogenation for cis, trans and vinyl butadiene segments was found to be

$$k_{cis} \simeq k_{trans} < k_{vinyl}.$$

II. Recommendations

A. Future research on polycyclohexadiene microstructure. 1,2- vs. 1,4-diene addition in the polymerization of 1,3-CHD was characterized by interpreting changes

in the C-H out-of-plane stretching bands in the infrared spectra of model cis olefins as related to similar bands observed in the infrared spectra of the polymers as a function of polymerization reaction conditions. These stretching vibrations appear in the polymer spectra as multiple, overlapped bands, making quantitative interpretation difficult and subject to error. It is recommended that carbon-13 nmr analysis, which is directly sensitive to the makeup of the chain backbone, be used to confirm or modify the interpretations of the present infrared data.

B. Future research on diimide hydrogenation of polymer substrates. Diimide hydrogenation of olefins conducted at lower temperatures (e.g., 25°C) produces selective cis, trans, and vinyl hydrogenation in the order cis $<$ trans $<$ vinyl. Thus, it may be interesting to attempt polymer-diimide hydrogenations with the ortho, meta, and para-nitro derivatives of benzenesulfonylhydrazide which are known to generate diimide at temperatures as low as 25°C. If successful, the technique could be used to synthesize novel ethylene-cis-butadiene copolymers using cis-trans polybutadiene copolymers as precursors. From a more fundamental viewpoint, the method could be useful as a characterization tool. Cis-trans polybutadienes made from the radiation-induced isomerization

of cis-polybutadiene might be selectively hydrogenated and the product studied by nmr to detect the sequence distribution of the precursor polymer. This distribution would be related to mechanistic details of the original cis ⟶ trans isomerization.

Further characterization of several aspects of the present diimide hydrogenation reaction with polymers may be useful. It is not known if the reagent hydrogenates the polymer chains in a random or block-like fashion. It may be possible to correlate the melting points (via DSC) of partially hydrogenated polybutadienes to per cent conversion to provide information in this area.

While some byproduct substitution apparently occurs in diimide hydrogenation with p-TSH, little quantitative information concerning these side reactions is available. It would be useful to confirm the nature of the byproduct reactions and quantitatively characterize the effects of substrate and reaction conditions on their extent. The possibility of controlling these side reactions by adding small amounts of a tertiary amine to the reaction system to tie up the reactive, acidic byproducts as inert salts should definitely be considered in future work. It should be noted, though, that organic amine-type bases must be used because stronger, inorganic bases would promote

diimide decomposition to inert materials.

A final area of future investigation might be characterization of molecular weight changes during diimide hydrogenation. This possibility has been considered for polyisoprene and polycyclohexadiene and should be explicitly studied for polybutadiene homo- and copolymers.

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APPENDIX 1

PRINCIPAL REAGENTS, SOLVENTS, POLYMERS, AND THEIR SOURCES

Solvents

benzene (GS or F, certified)

toluene (GS)

o-xylene (GS or B)

mesitylene (E)

n-hexane (GS)

cyclohexane (GS)

o-dichlorobenzene (F)

methanol (GS or F, certified)

tetrahydrofuran (F, certified)

diglyme (An)

decahydronapthlene (F, certified)

diphenyl ether (E)

carbon disulfide (F, spectrograde)

chlorobenzene (E)

Reagents

1,3-cyclohexadiene (C, 98% grade)

p-toluenesulfonylhydrazide (Ar or E)

titanium tetrachloride (F, purified)

1,cis-2-dimethylcyclohexane (CS, 99.9%)

1,trans-2-dimethylcyclohexane (CS, 99.9%)

3,6-dimethylcyclohexene (CS, 99%)

cis 1,4-dimethylcyclohexane (CS, 99%)

trans 1,4-dimethylcyclohexane (CS, 99%)

3,5-dimethylcyclohexene (CS, 99%)

boron trifluoride (M)

triisobutyl aluminum (TA)

vanadium trichloride (Af)

tetramethylethylenediamine (E)

carbon dioxide (M, bone dry)

cyclohexene (E)

cobalt acetyacetonate (Af)

n-butyllithium (Af or Fo)

1,4-cyclohexadiene (C)

2,5-dimethyl-2,4-hexadiene (K)

2,5-dimethylcyclohexanol (C)

3,4-dimethylcyclohexanol (CS)

magnesium sulfate

Polymers

cis-1,4-polybutadiene (P)

cis-1,4-polyisoprene (BFG)

trans-1,4-polybutadiene (P)

methyl rubber (K/K)

styrene-butadiene random copolymer (GT)

polychloroprene

styrene-butadiene-styrene

poly(2,5-dimethyl-2,4 hexadiene)

Sources

P = Phillips Petroleum Co.

An = Ansul

S = Shell

M = Matheson

GT = General Tire + Rubber

Ar = Aldrich

BFG = B. F. Goodrich

Af = Alfa Inorganic

B = Baker

Fo = Foote Mineral

F = Fisher

TA = Texas Alkyls

E = Eastman

CS = Chemical Samples Co.

GS = General Stocks

C = Columbia

K = K/K Chem.

APPENDIX 2

CUSTOM MADE GLASSWARE

Figure 2a. Serum Capped Cylinder Reactor

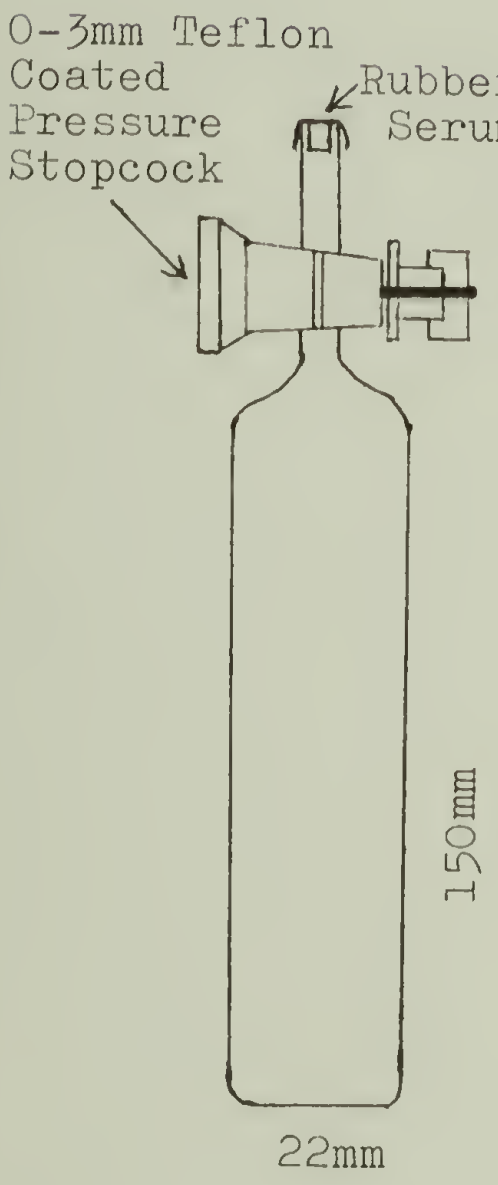
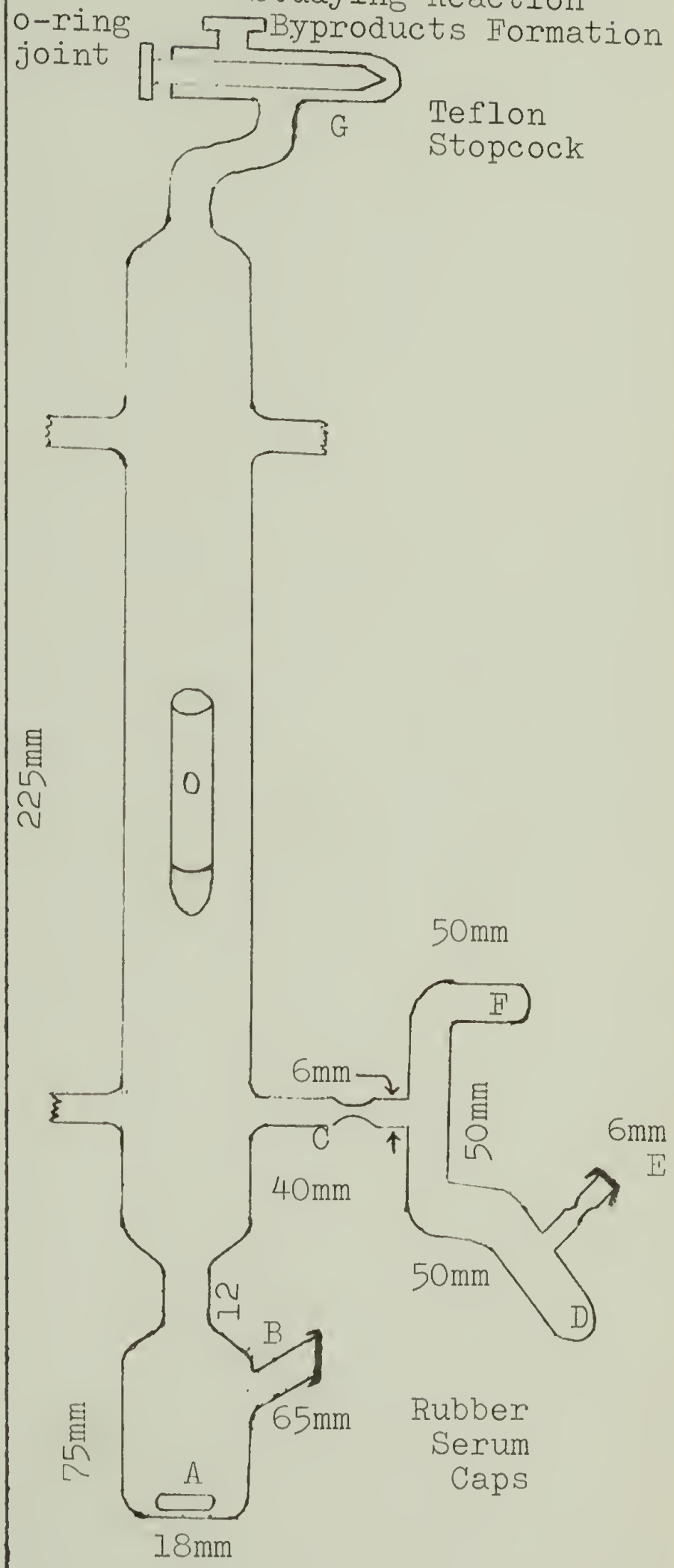
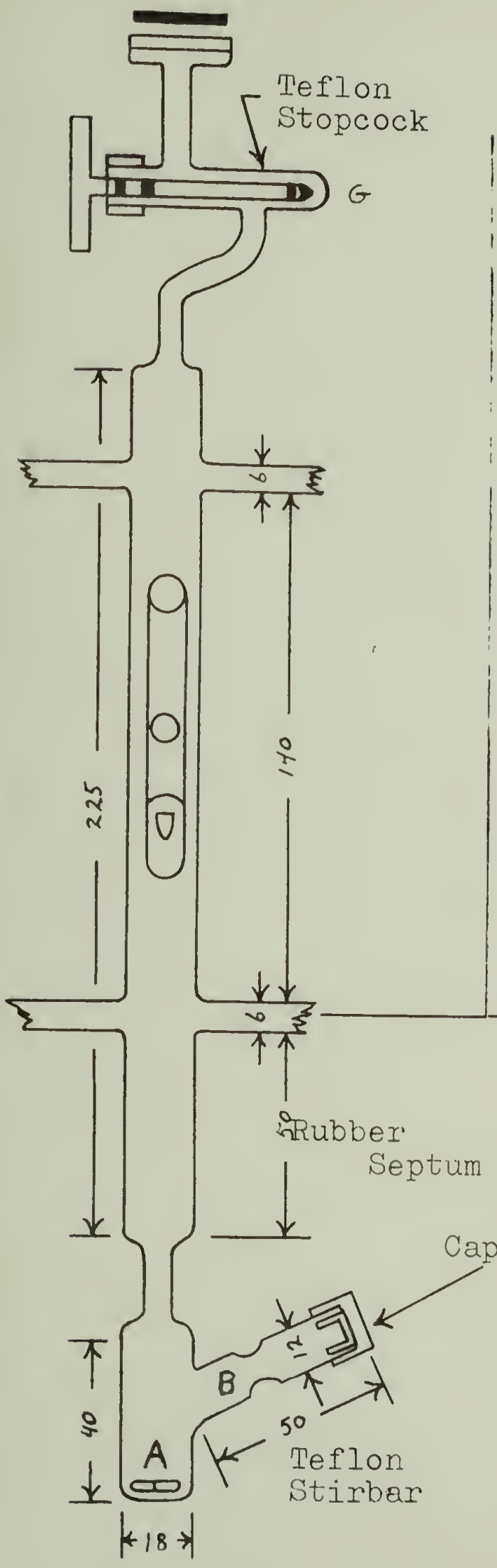


Figure 3. Apparatus Used for Studying Reaction Byproducts Formation

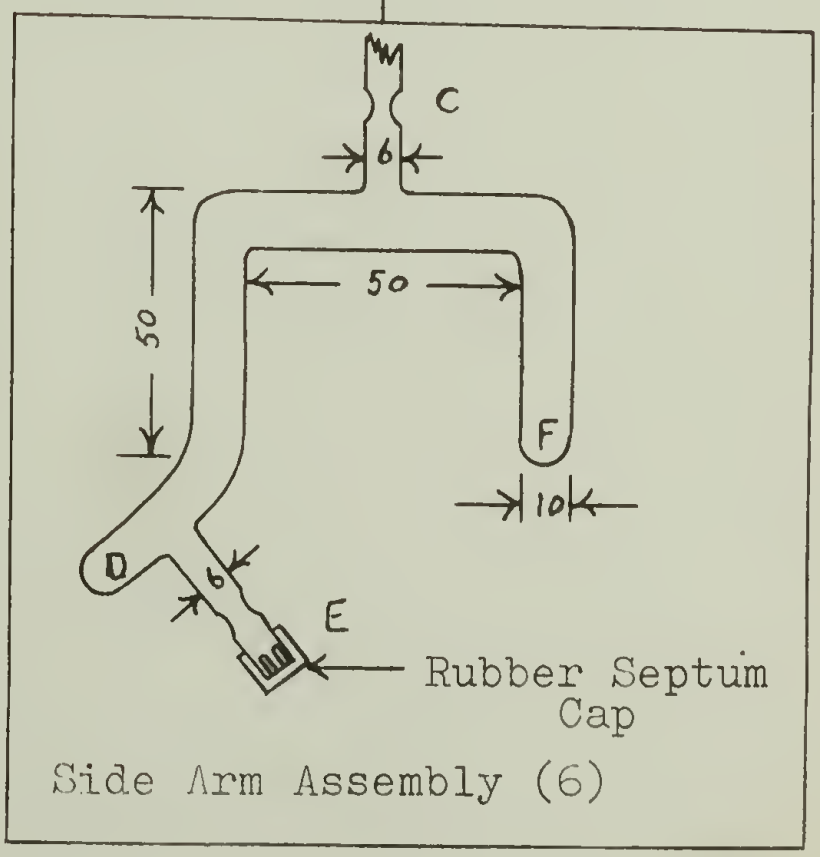


APPARATUS FOR STUDYING REACTION BYPRODUCTS IN THE ANIONIC POLYMERIZATION OF 1,3-CYCLOHEXADIENE



All Dimentions in MM.

Scale = 1/2



Side Arm Assembly (6)

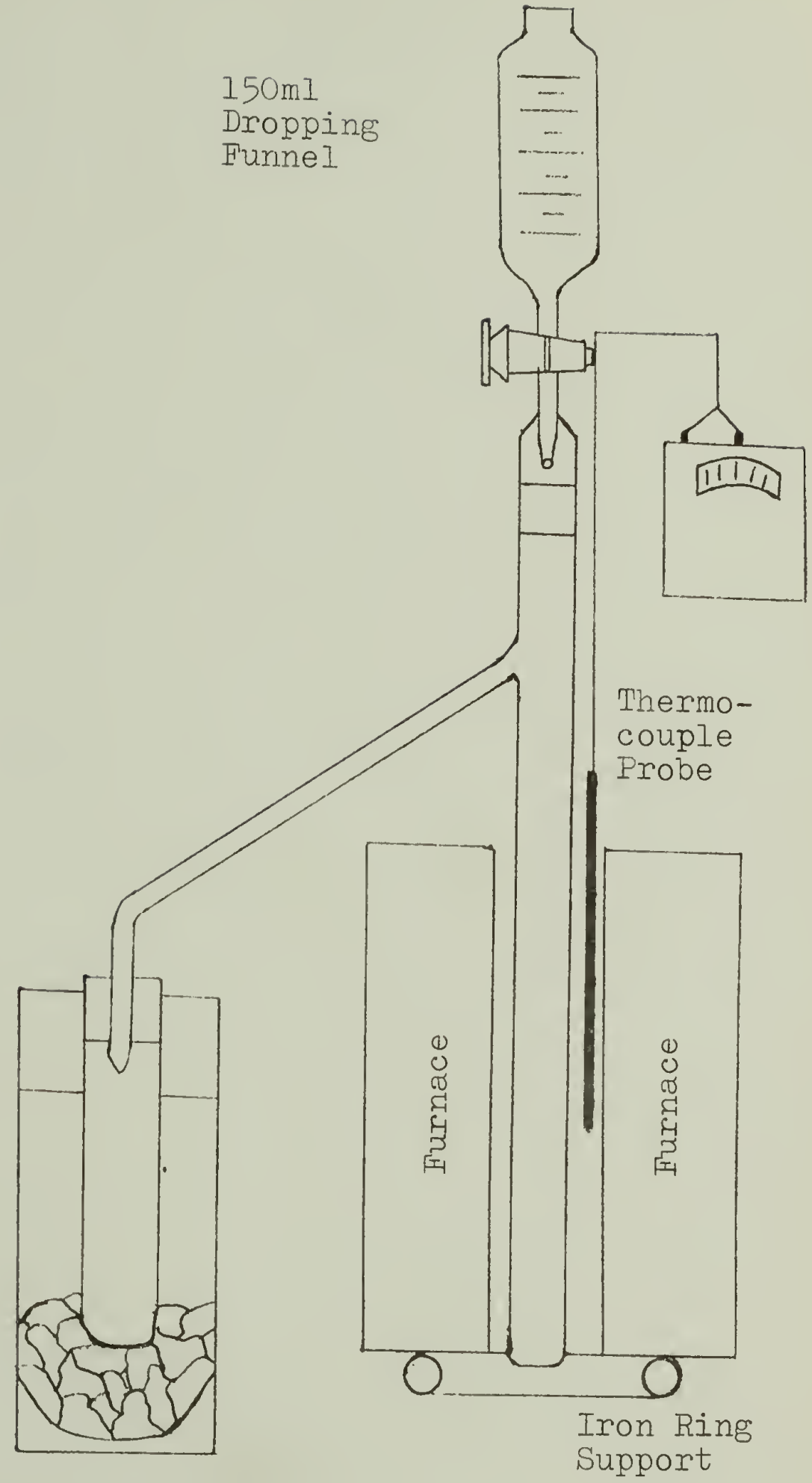
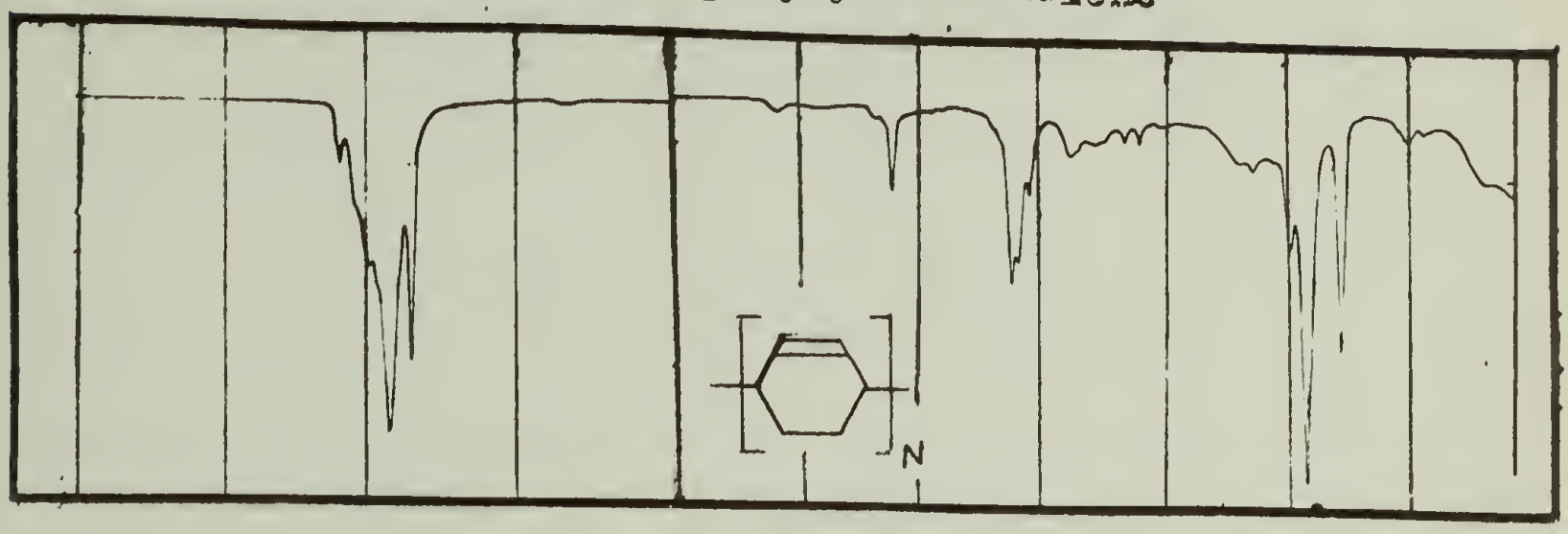


Figure 4. Pyrolysis Apparatus

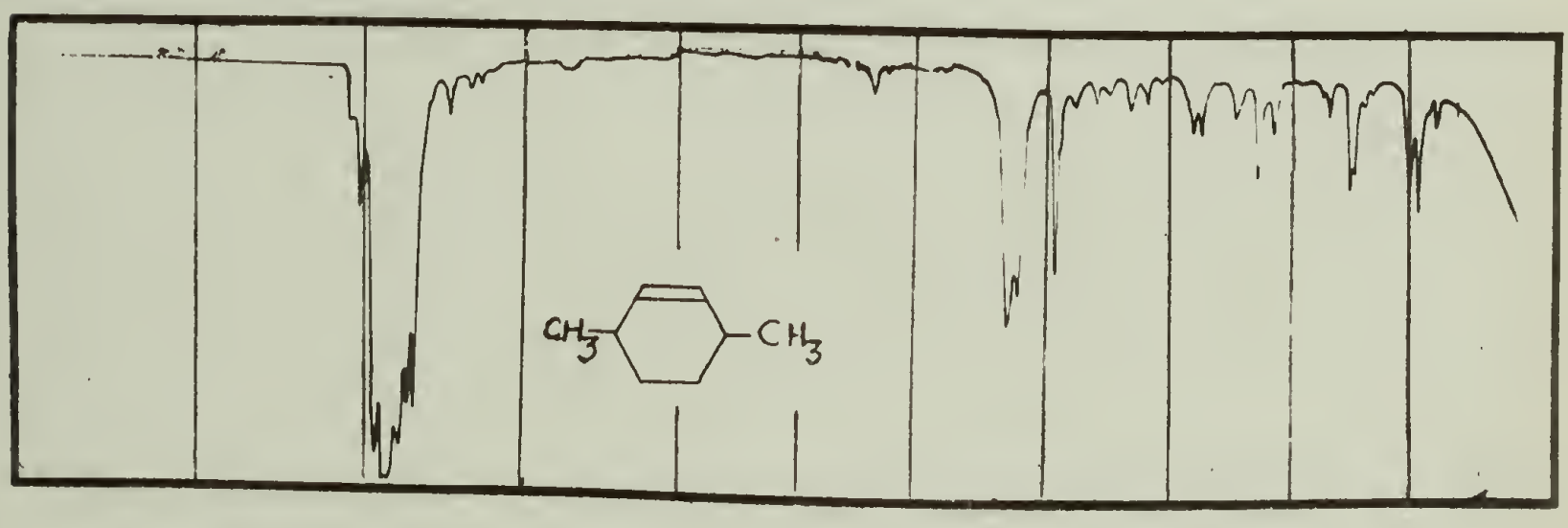
APPENDIX 3

INFRARED SPECTRA

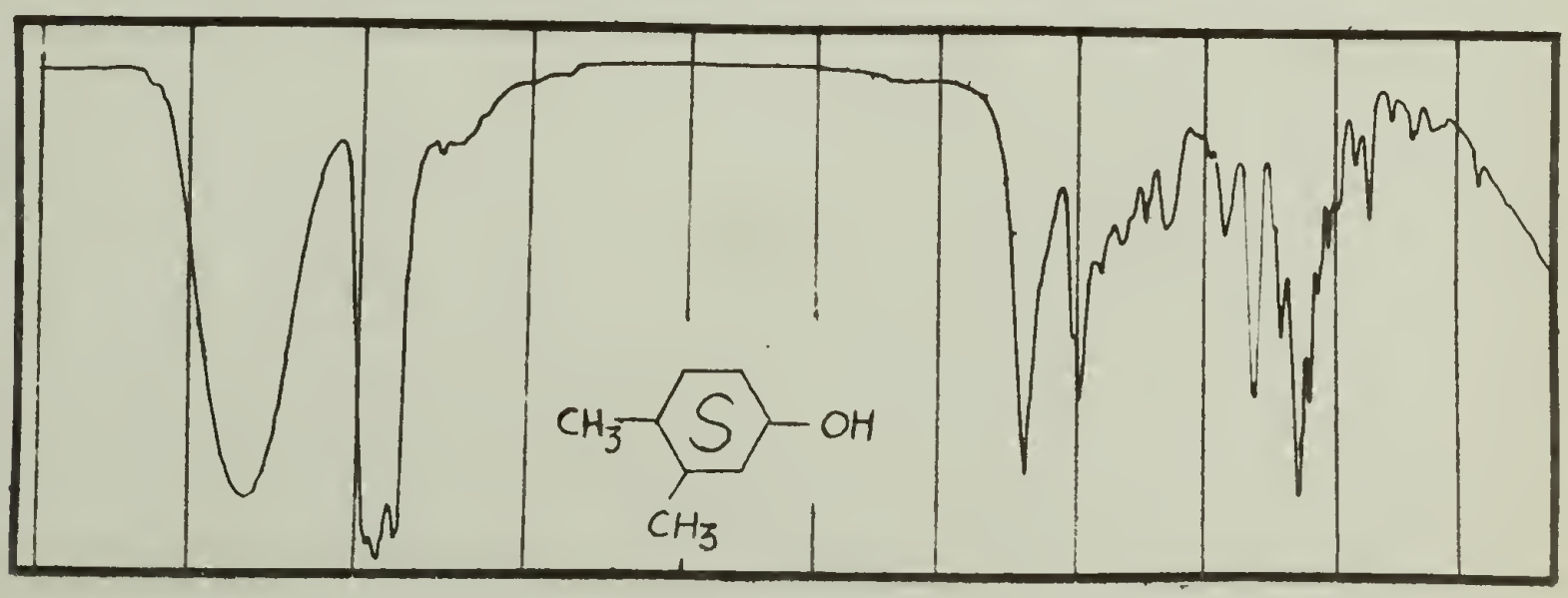
IR- 1. Alfin-polymerized polycyclohexadiene



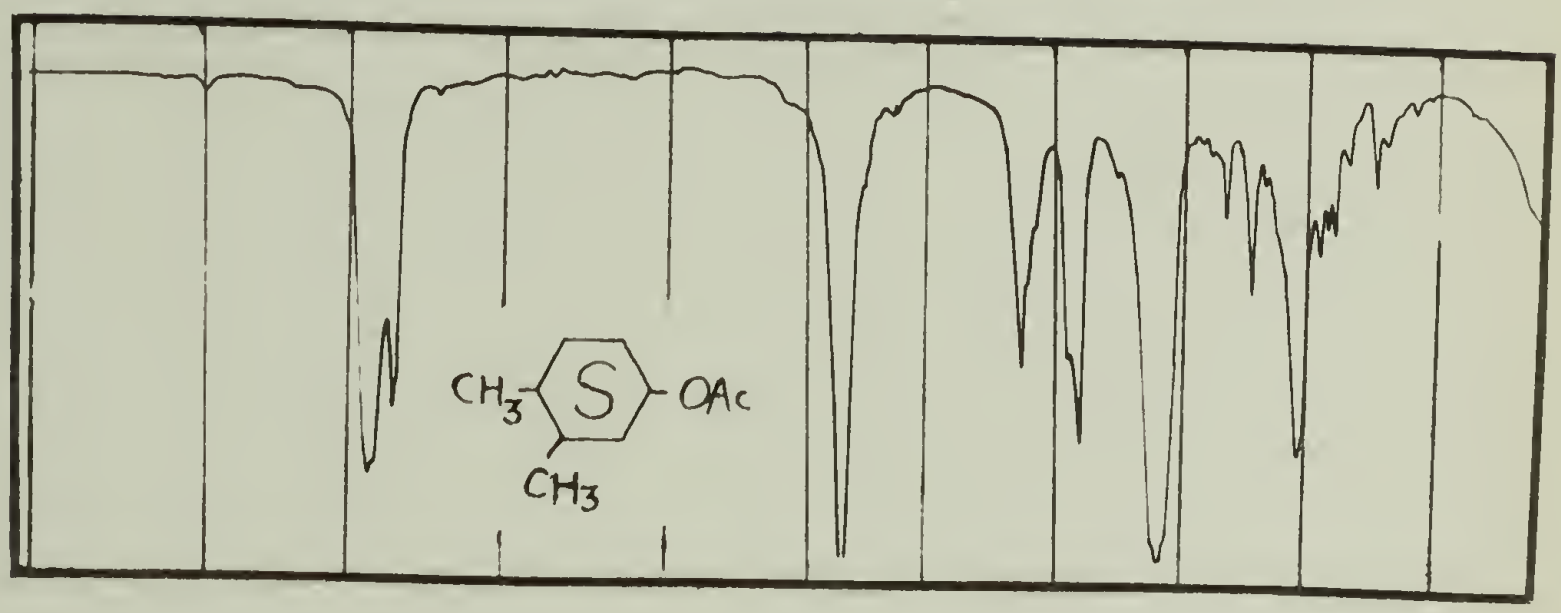
IR- 2. 3,6-dimethylcyclohexene



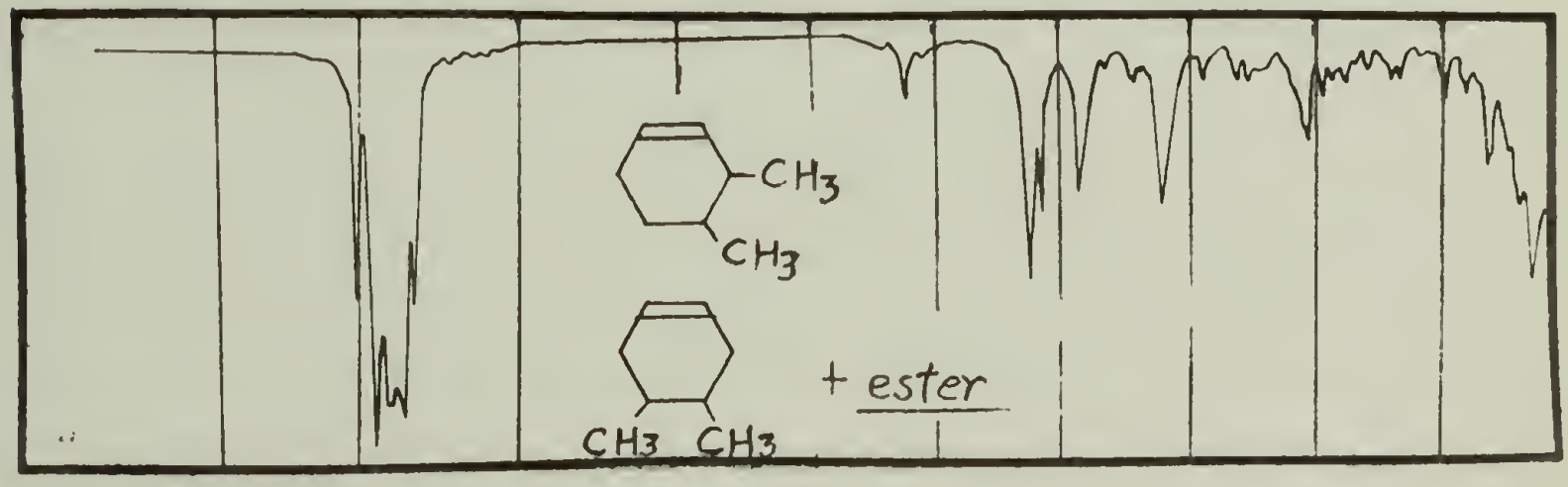
IR- 3. 2,3-dimethylcyclohexanol



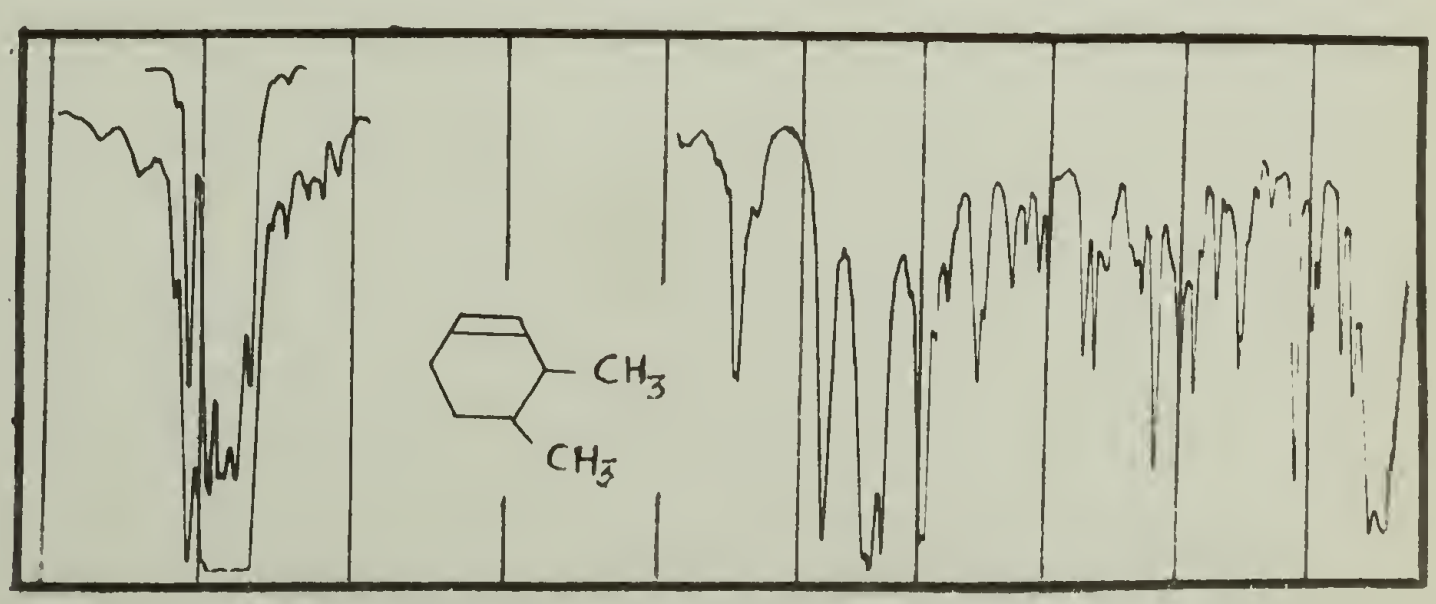
IR- 4. 2,3-dimethylcyclohexyl acetate



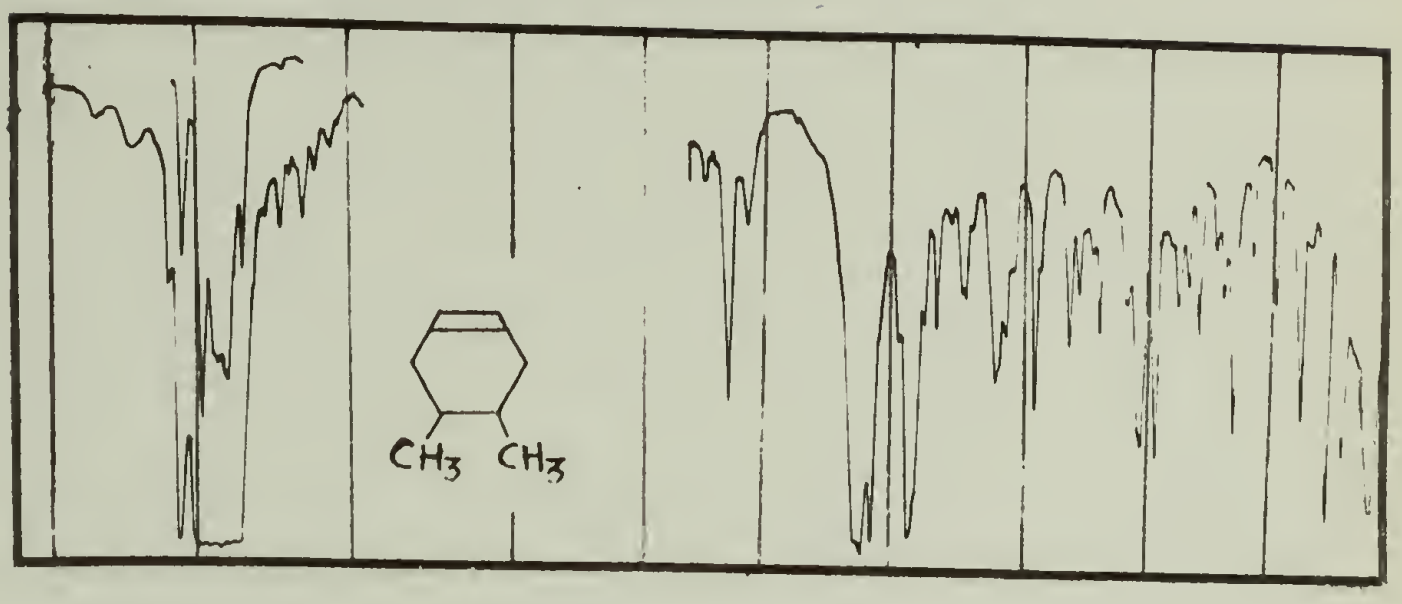
IR- 5. 3,4- and 4,5-dimethylcyclohexenes



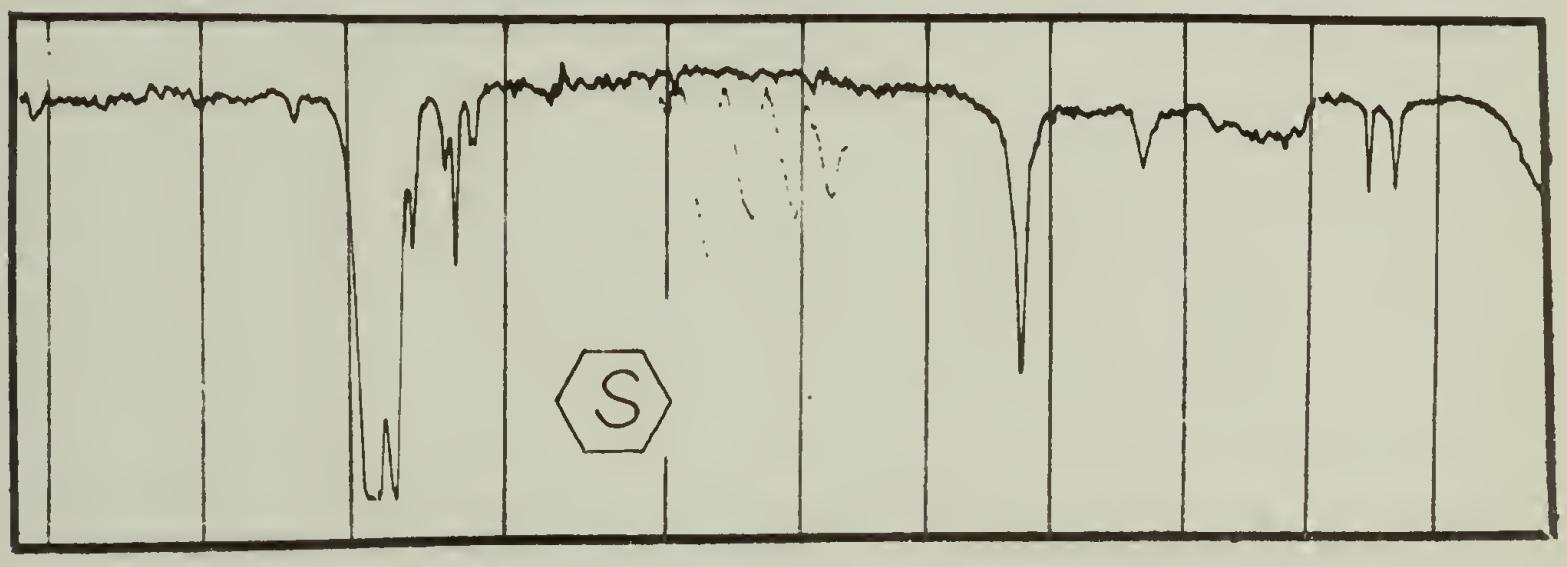
IR- 6. 3,4-dimethylcyclohexene



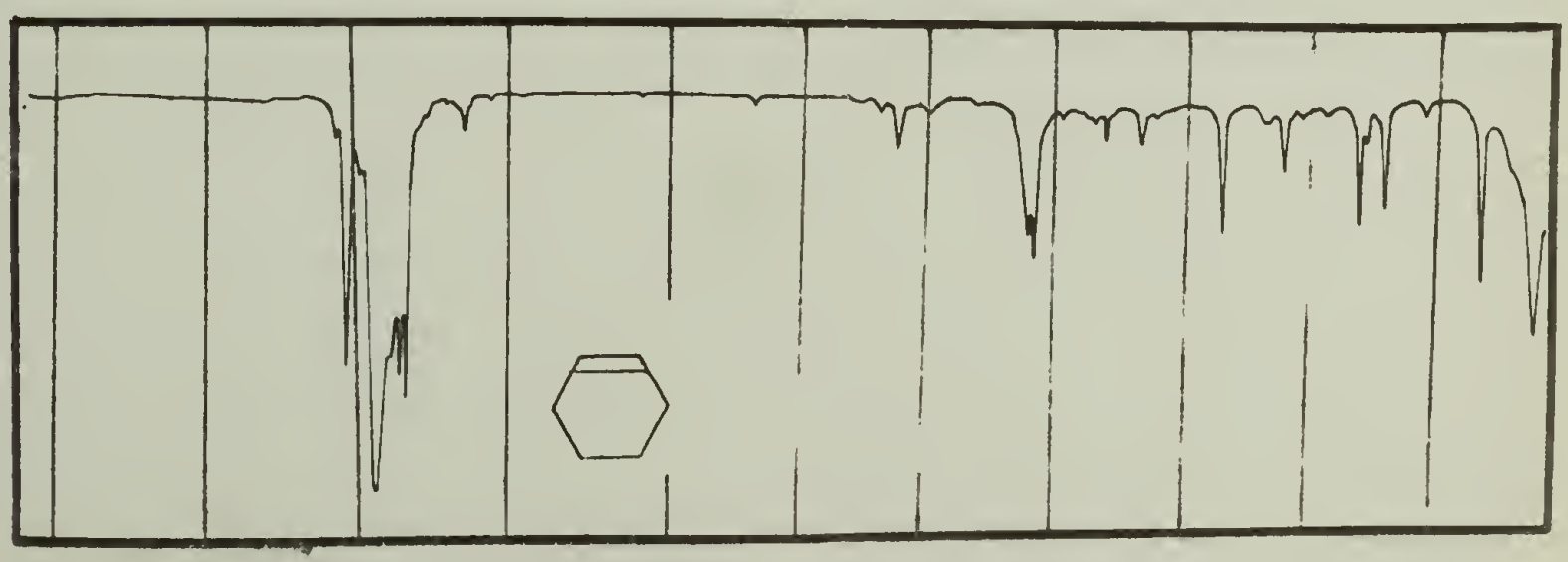
IR- 7. 4,5-dimethylcyclohexene



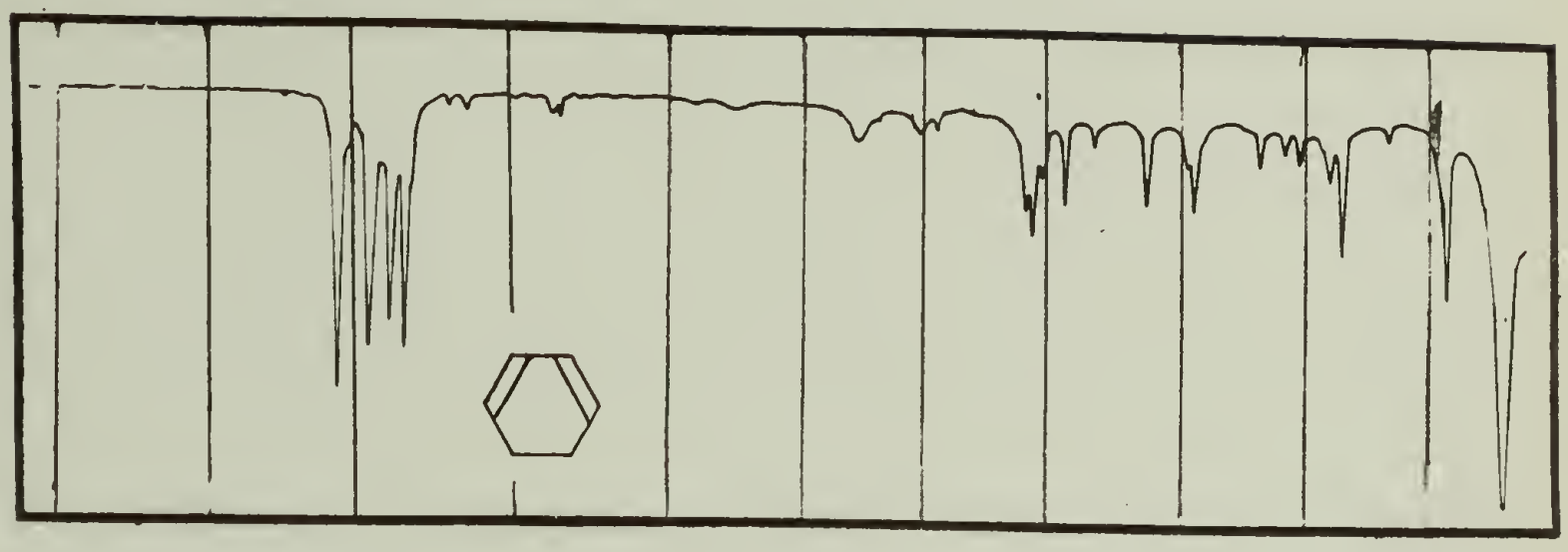
IR- 8. Cyclohexane



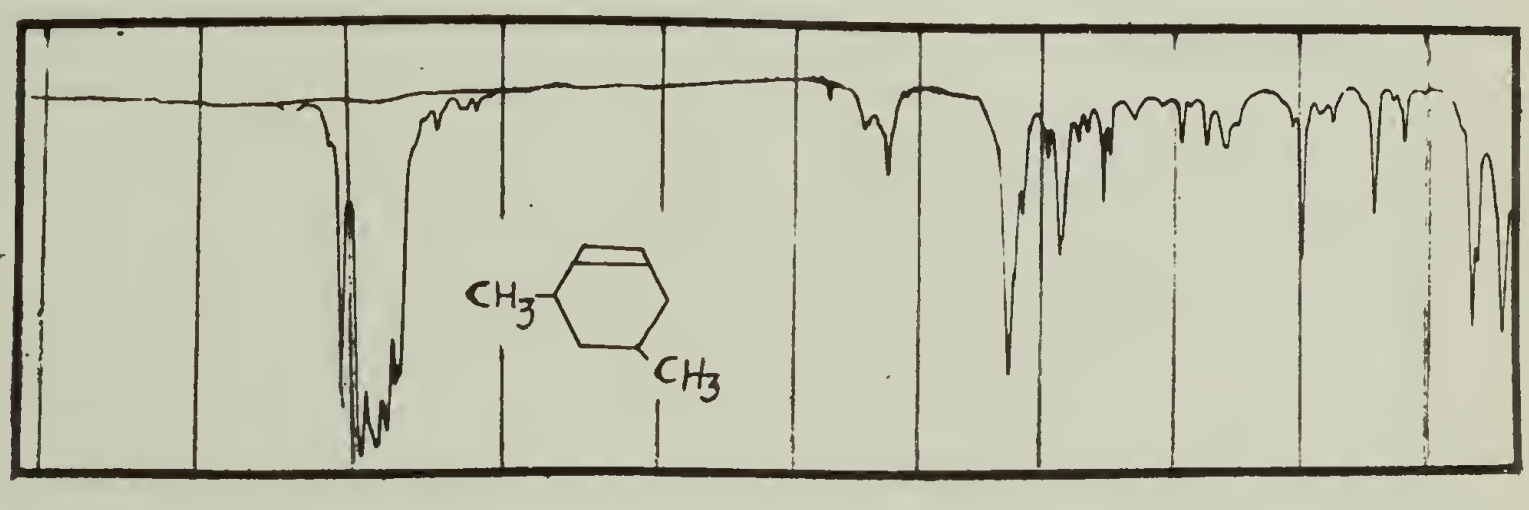
IR- 9. Cyclohexene



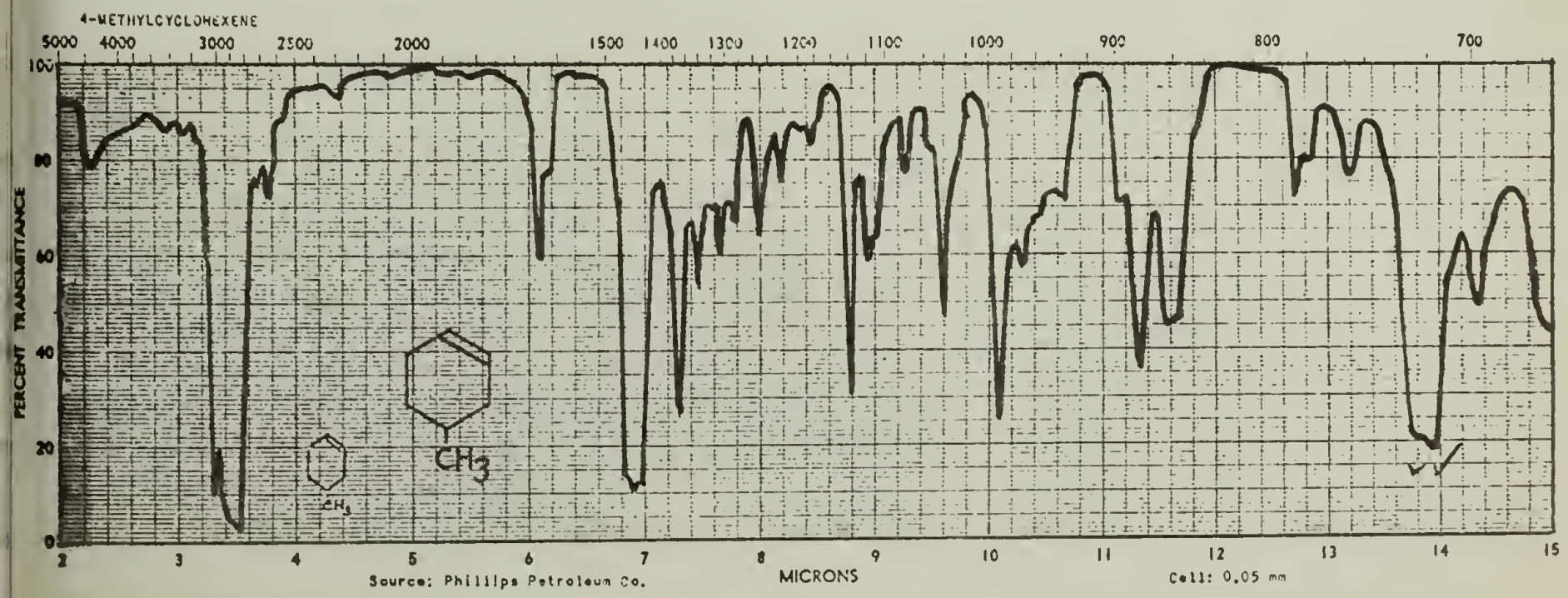
IR-10. 1,3-cyclohexadiene



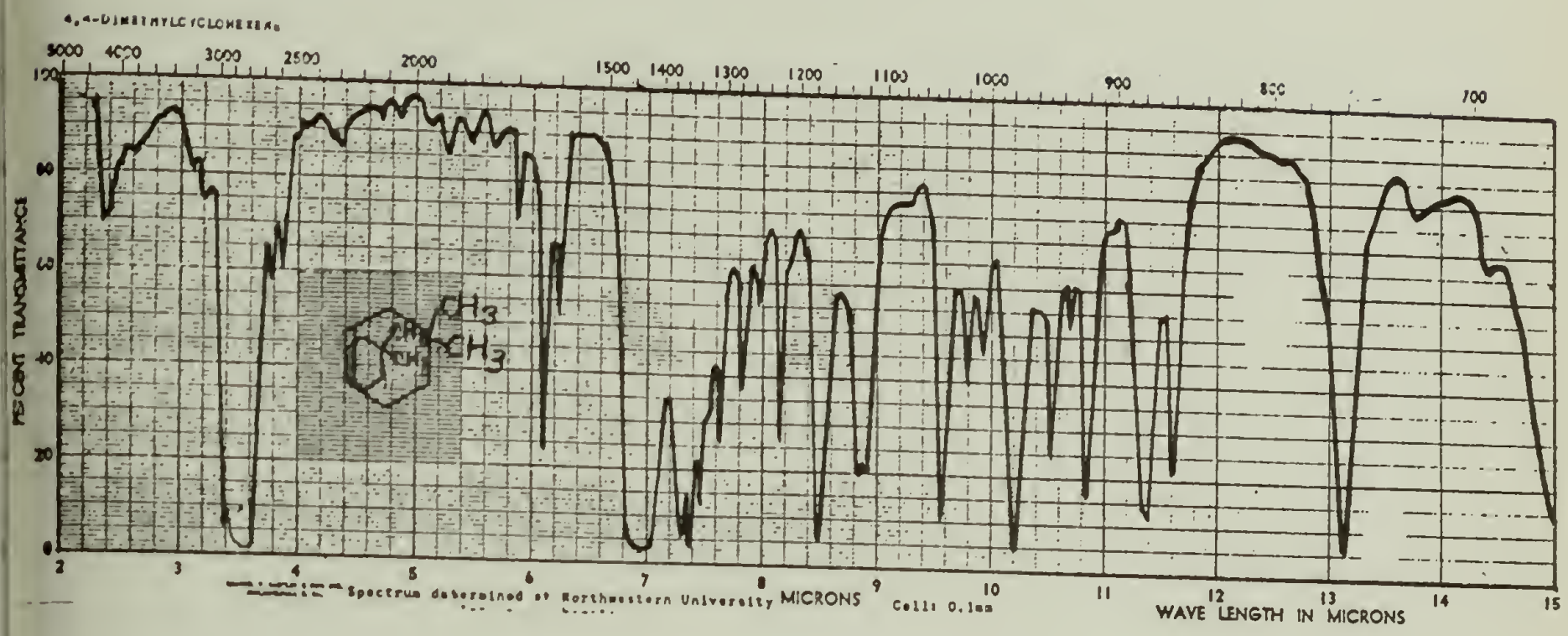
IR-11. 3,5-dimethylcyclohexene



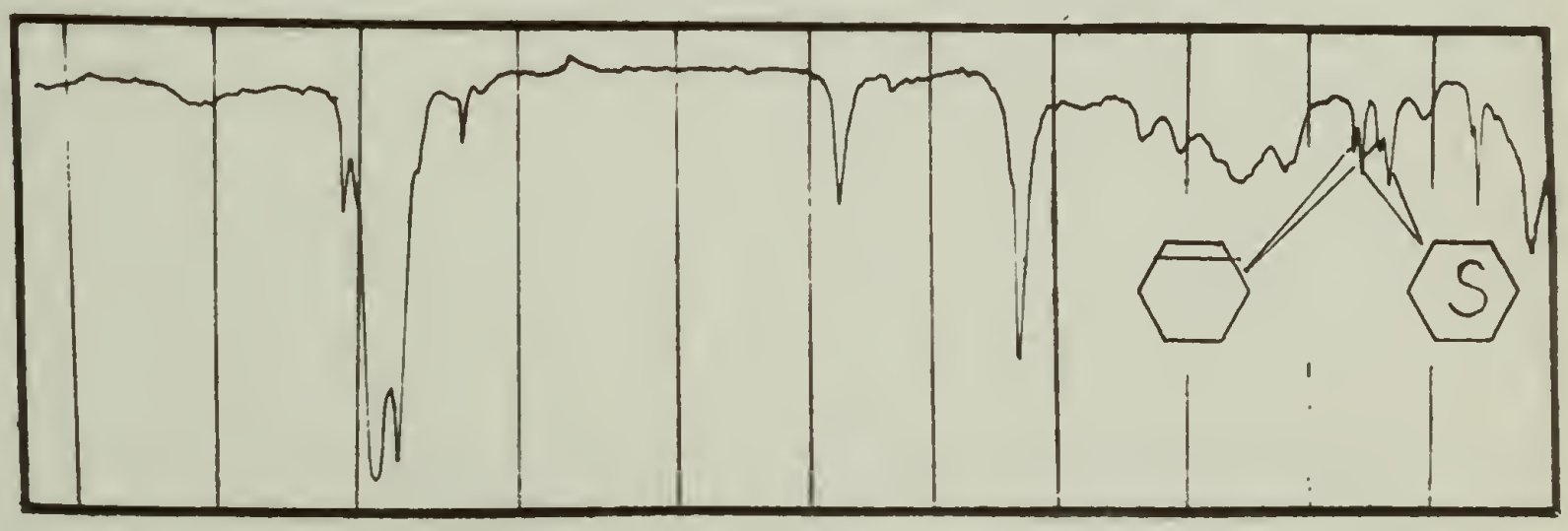
IR-12. 4-methylcyclohexene

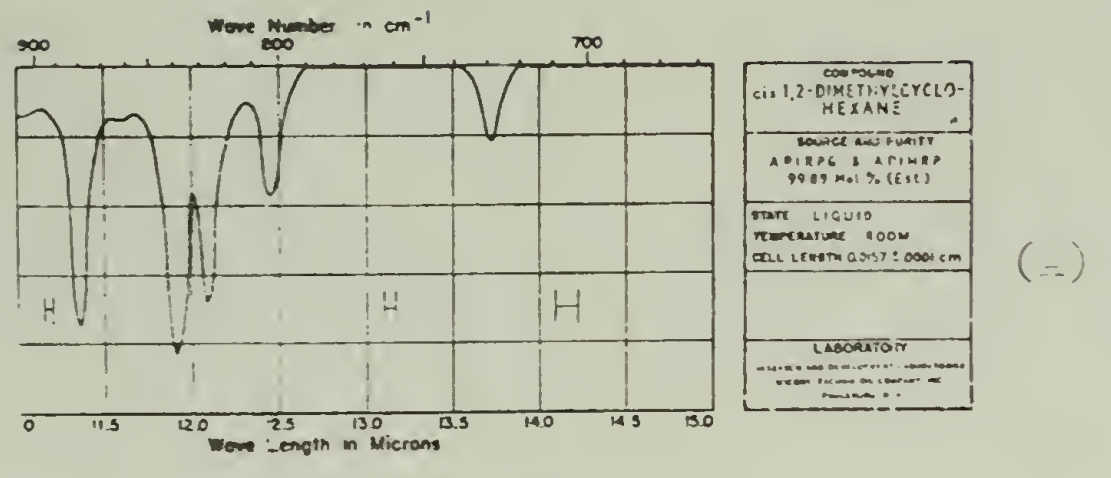


IR-13. 4,4-dimethylcyclohexene

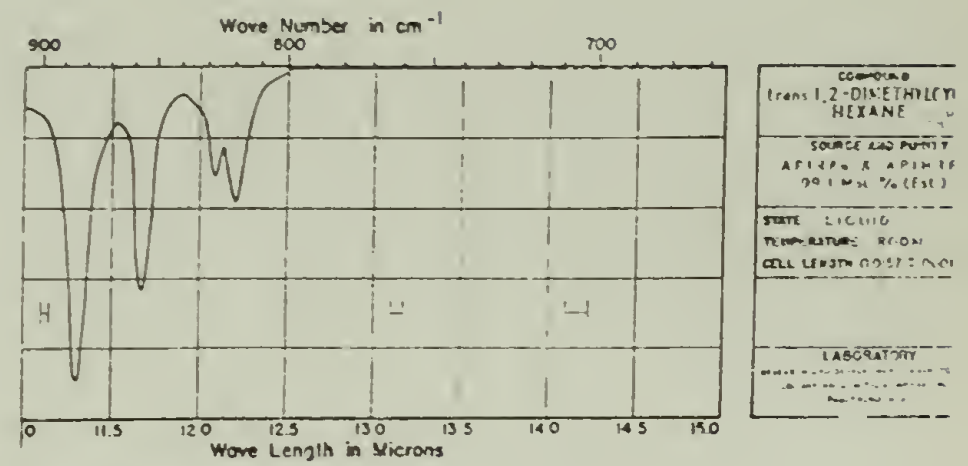


IR-15. Hydrogenation of cyclohexene with diimide

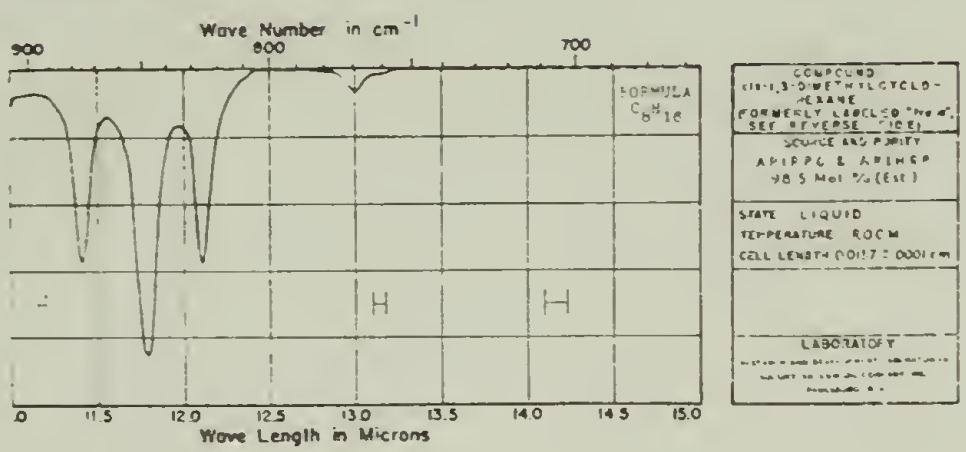




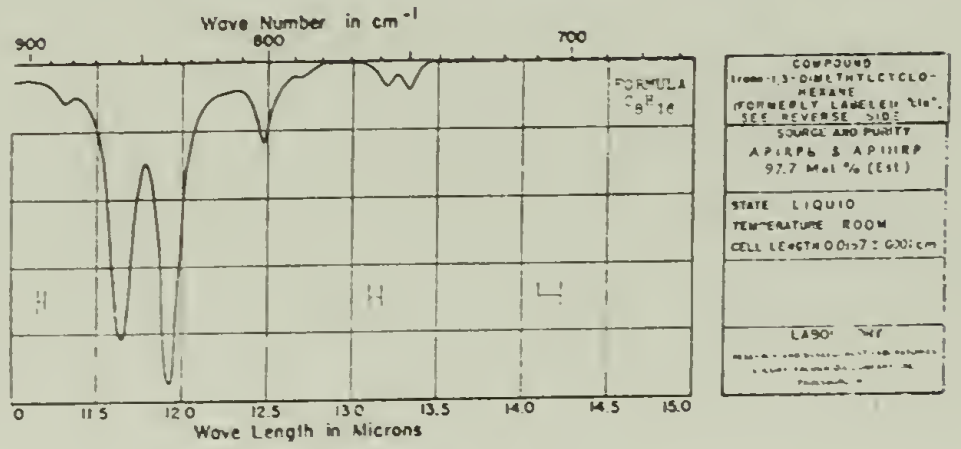
(A)



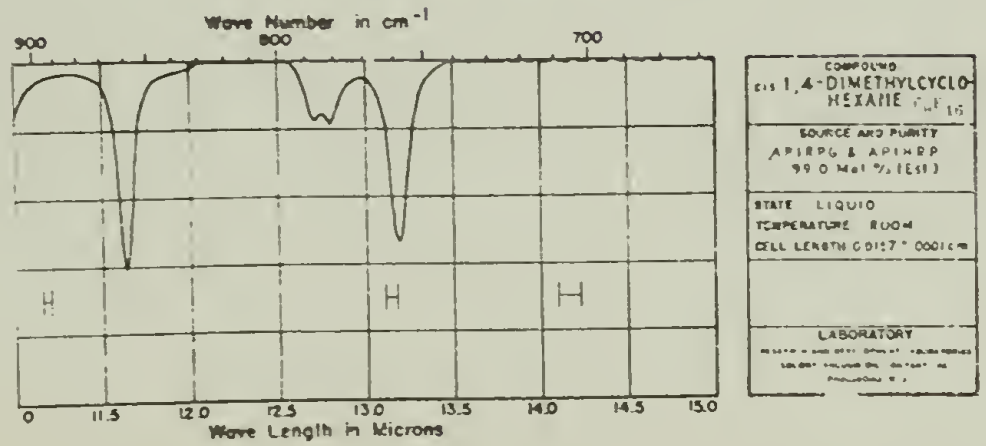
(B)



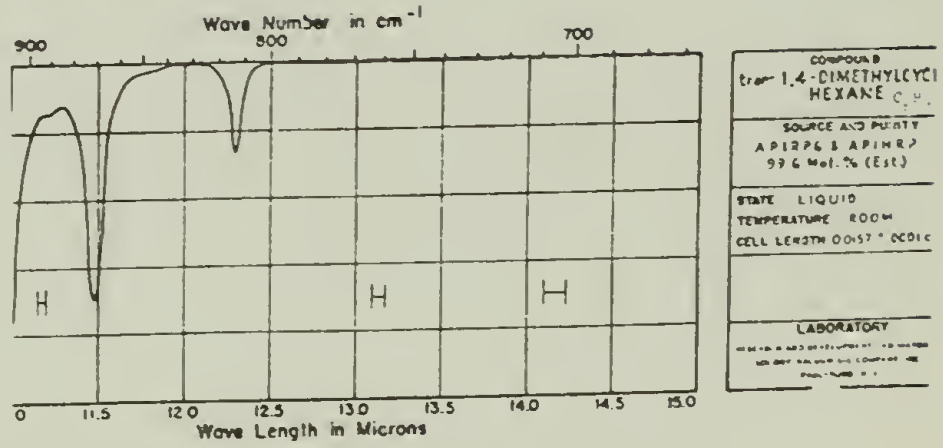
(C)



(D)



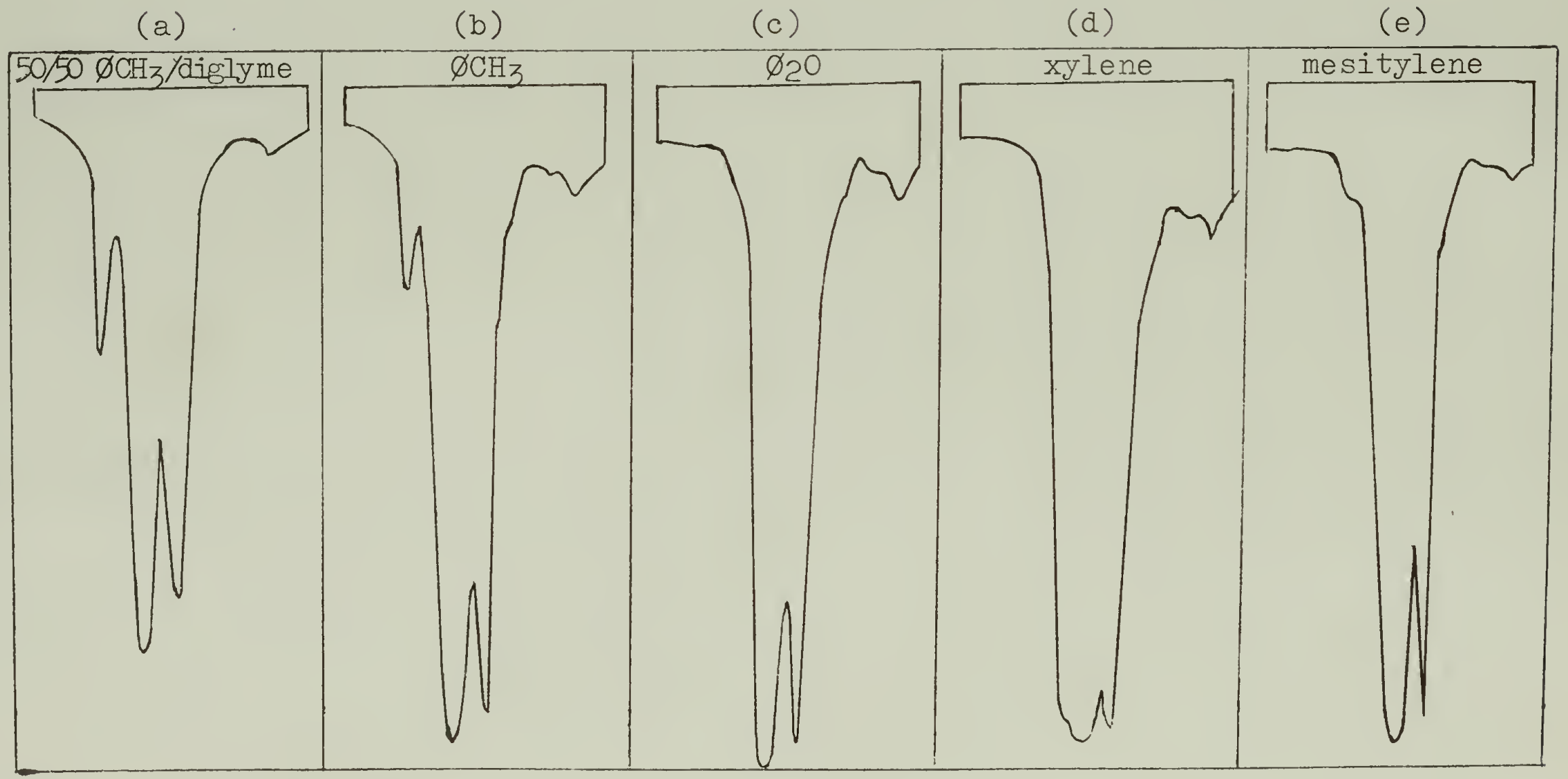
(E)



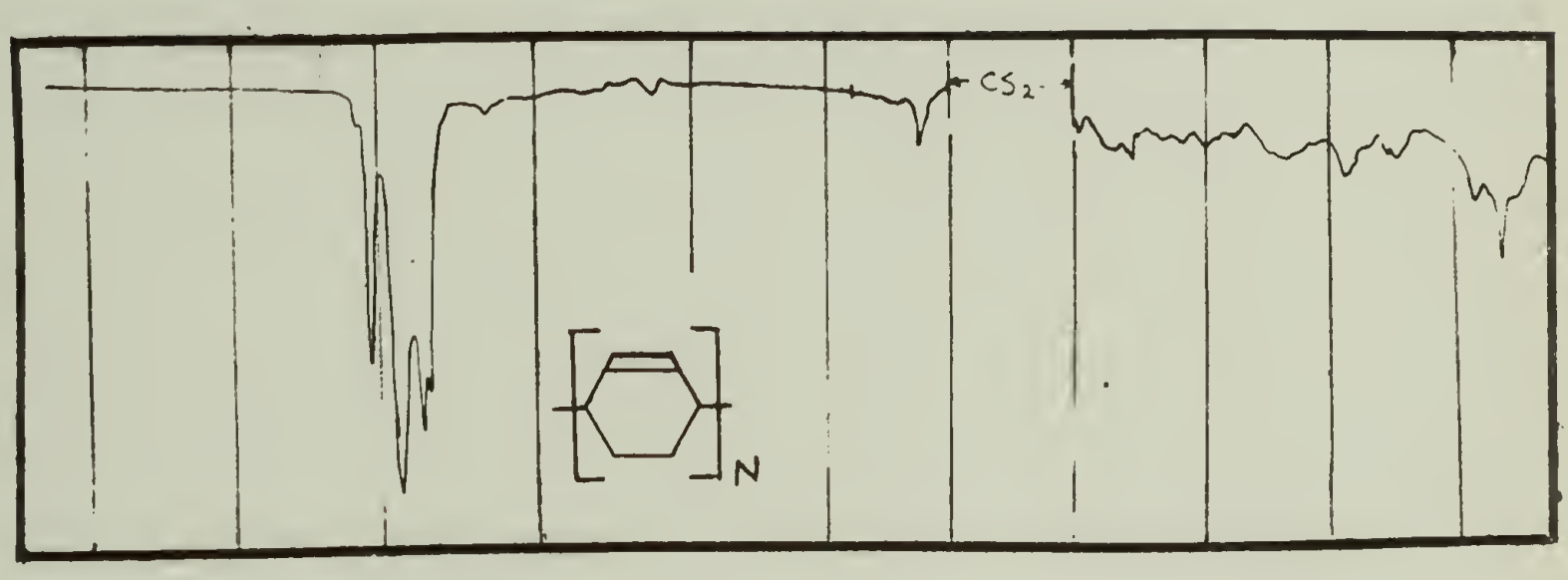
(F)

IR 14 a,f. cis and trans dimethylcyclohexanes; 625-900 cm^{-1} region.

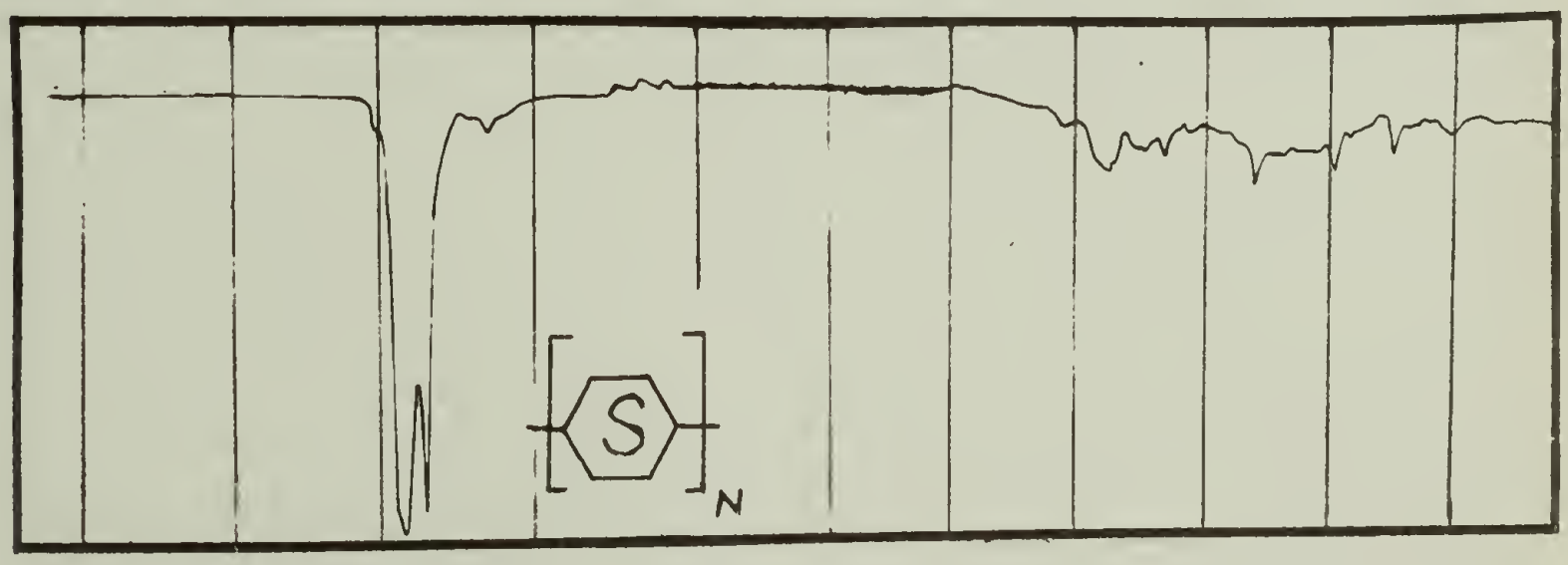
IR-16a,e. Reduction of the 3015 cm^{-1} vinyl band of polycyclohexadienes hydrogenated with diimide in various solvent media.



IR-17. Polycyclohexadiene

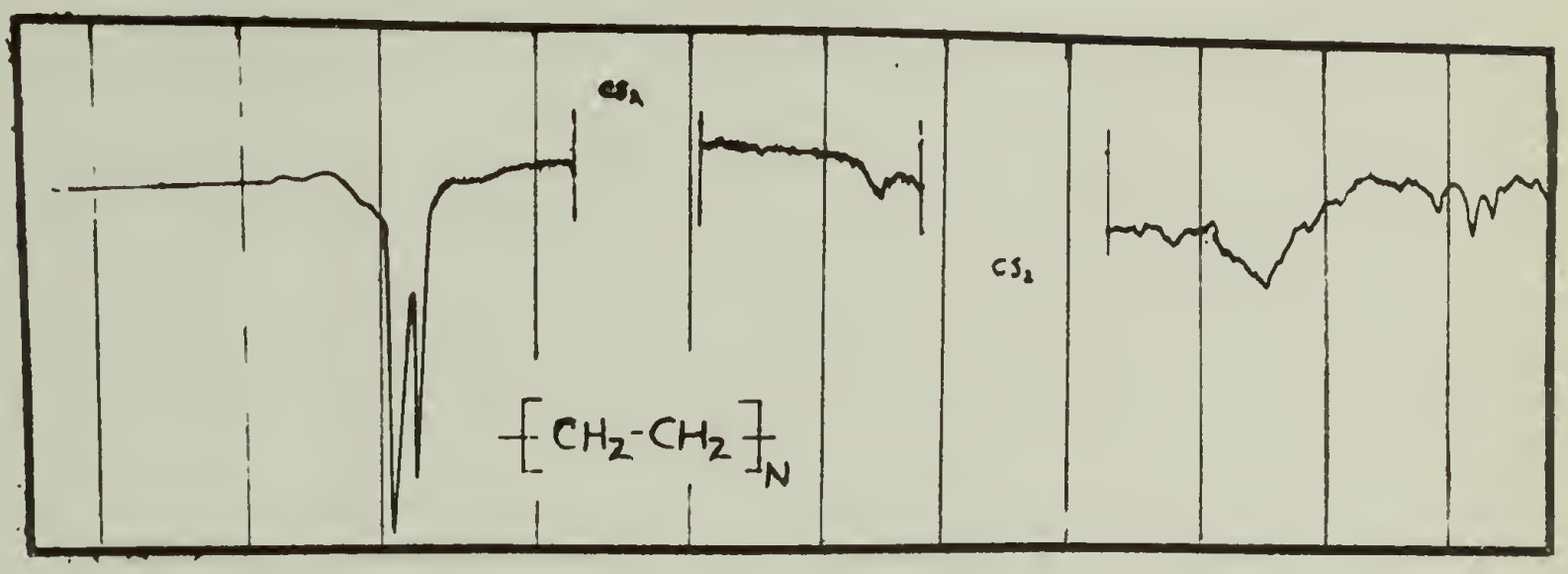


IR-18. Polycyclohexane

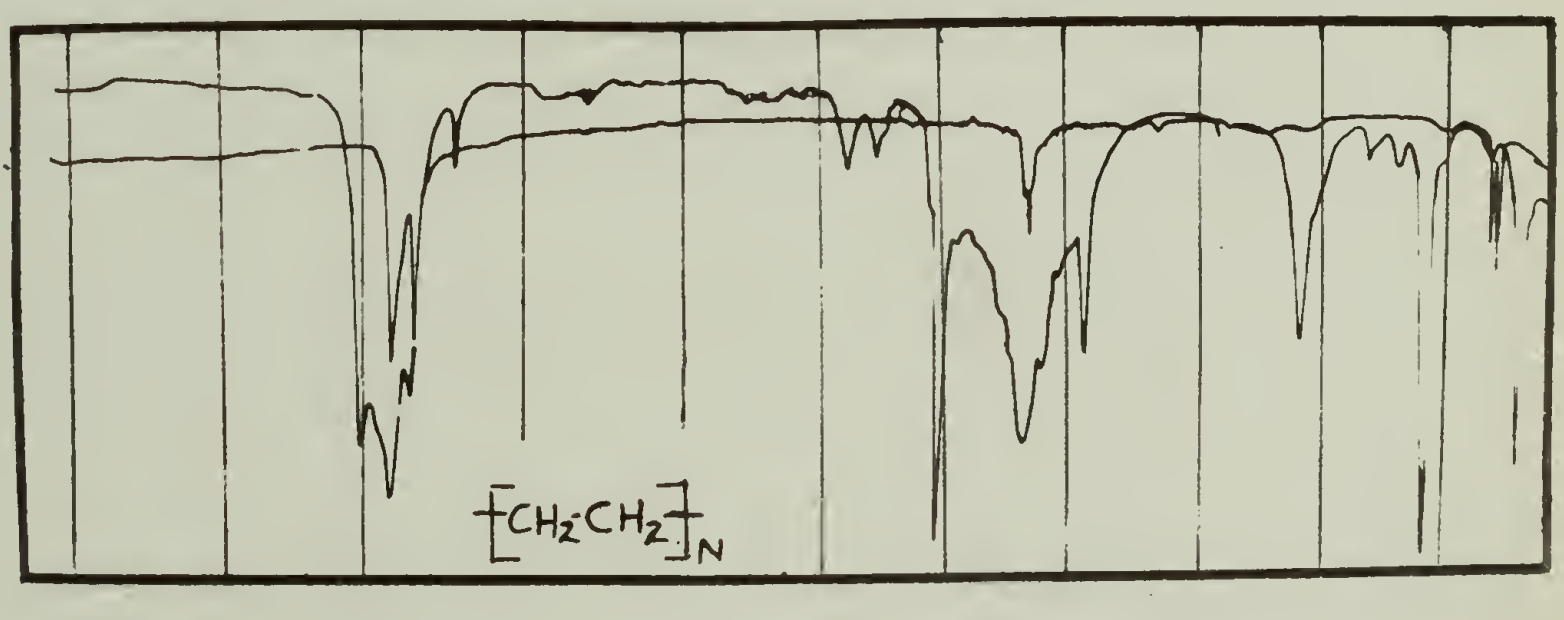


IR-19a,c. Products of the hydrogenation of polybutadiene with diimide in various media

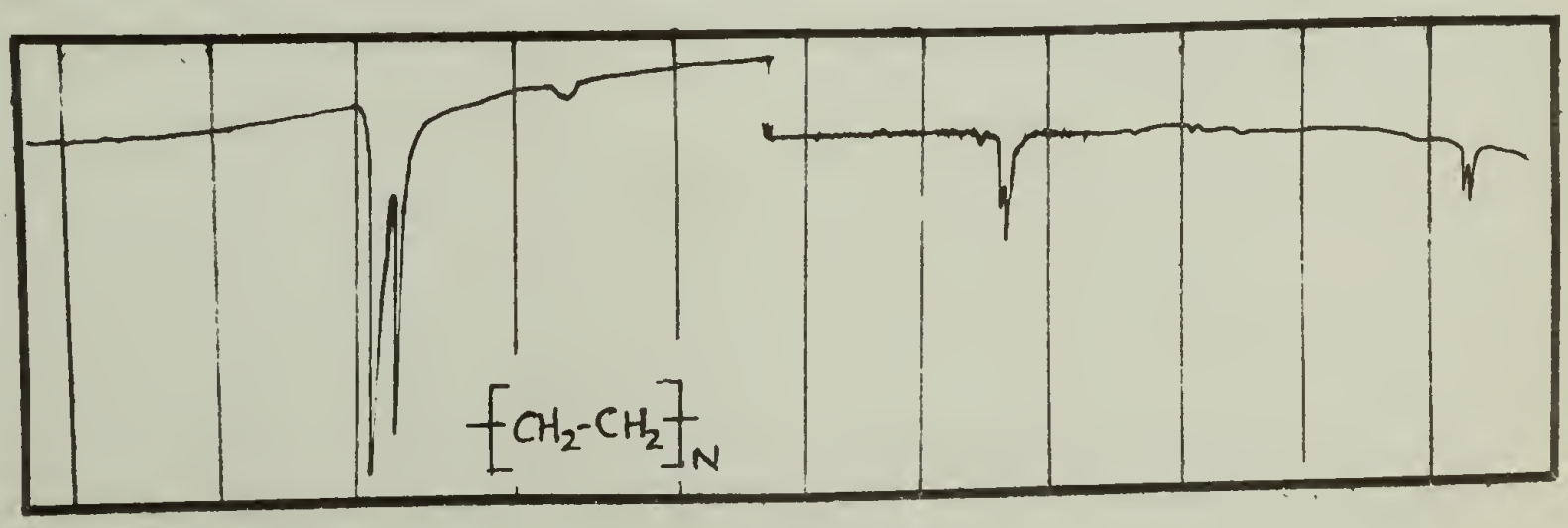
IR-19a. Hydrogenation in diphenyl ether



IR-19b. Hydrogenation in mesitylene

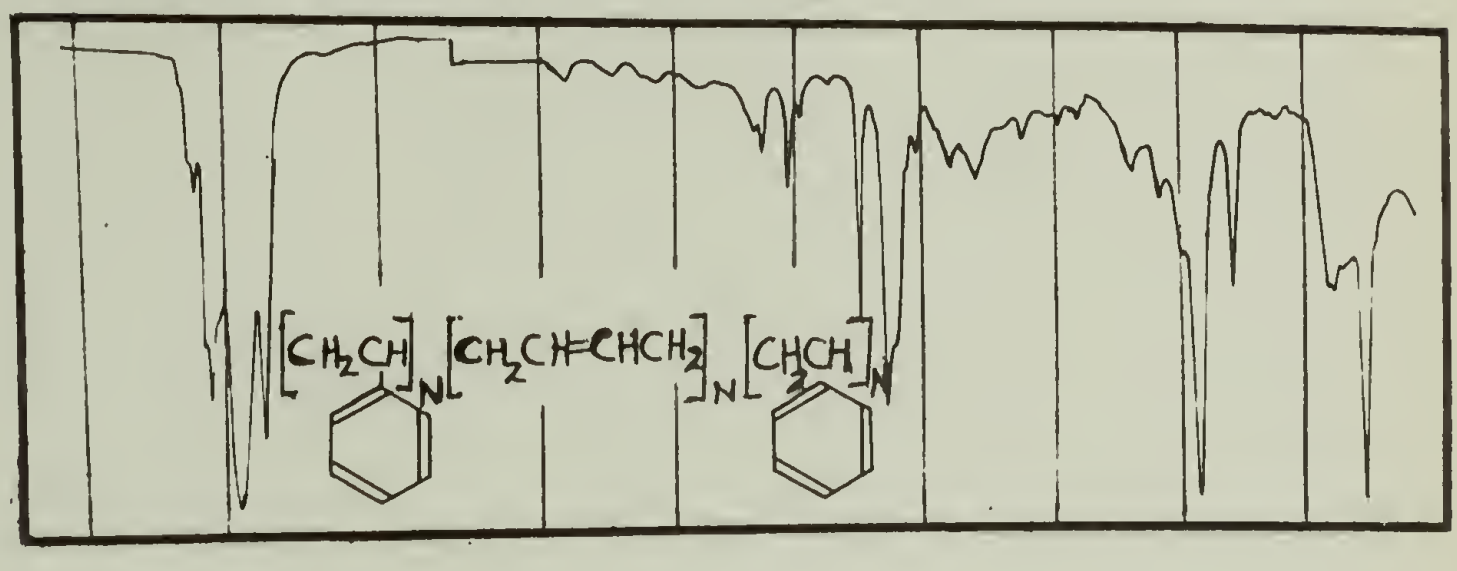


IR-19c. Hydrogenation in xylene

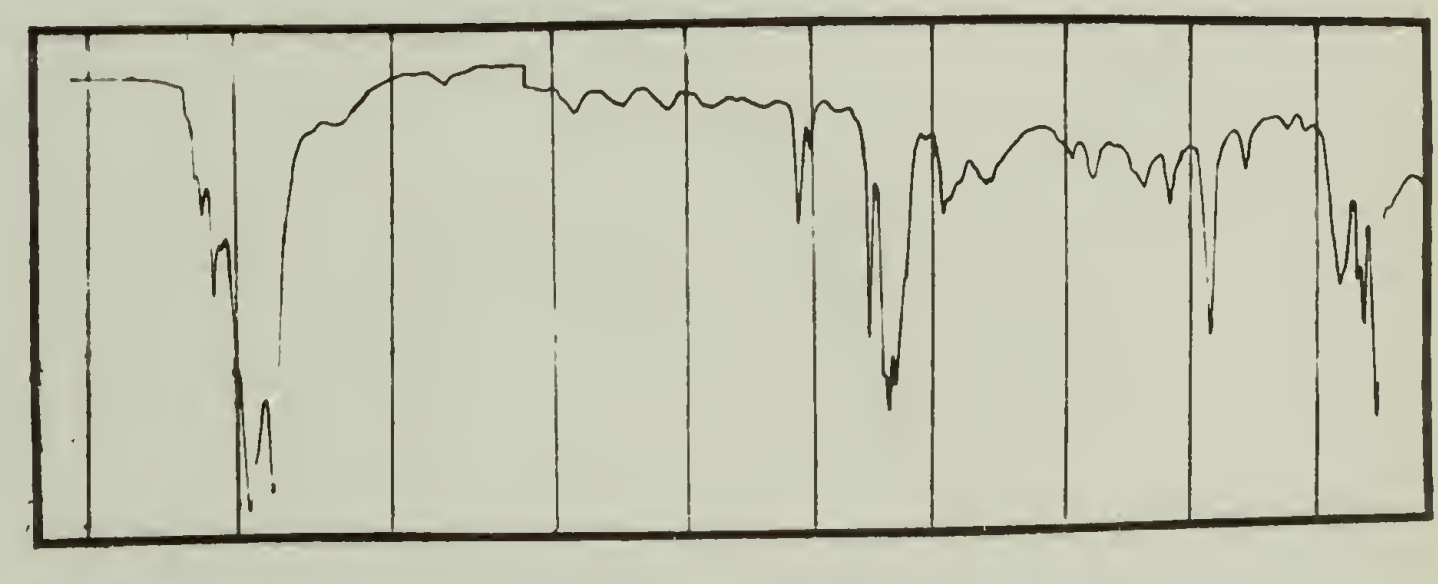


IR-20a,c. Styrene-Butadiene-Styrene block copolymers at various stages of hydrogenation by diimide

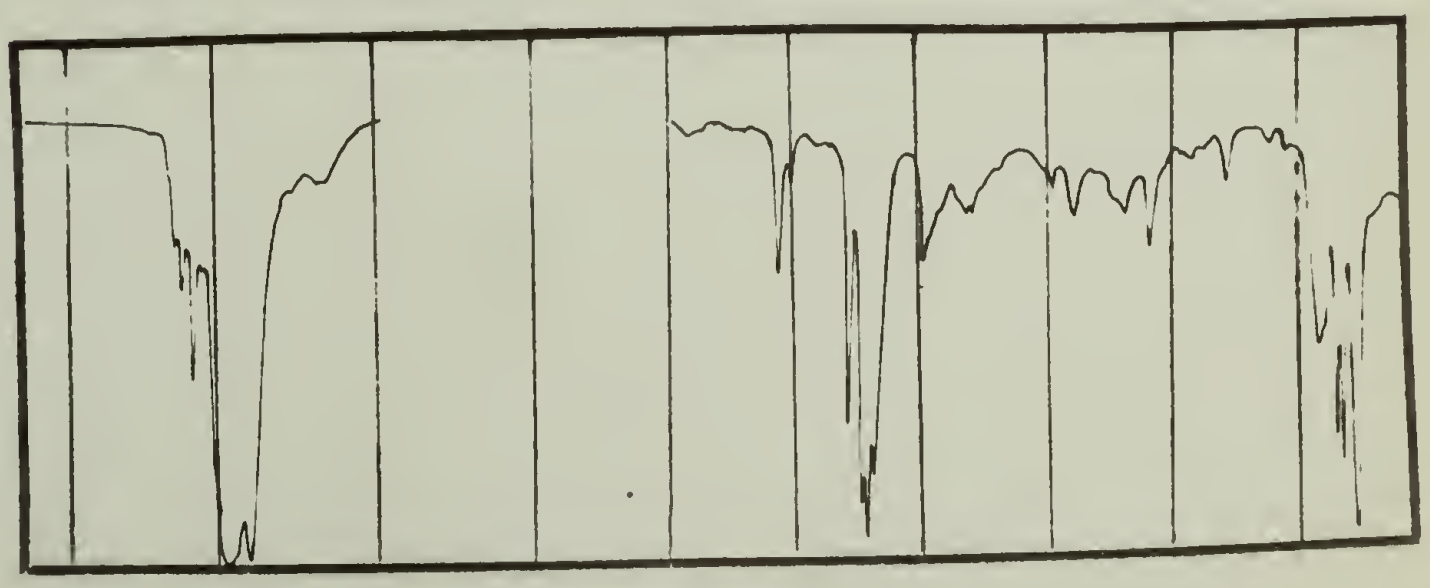
IR-20a. SBS-B-1 copolymer (starting material)



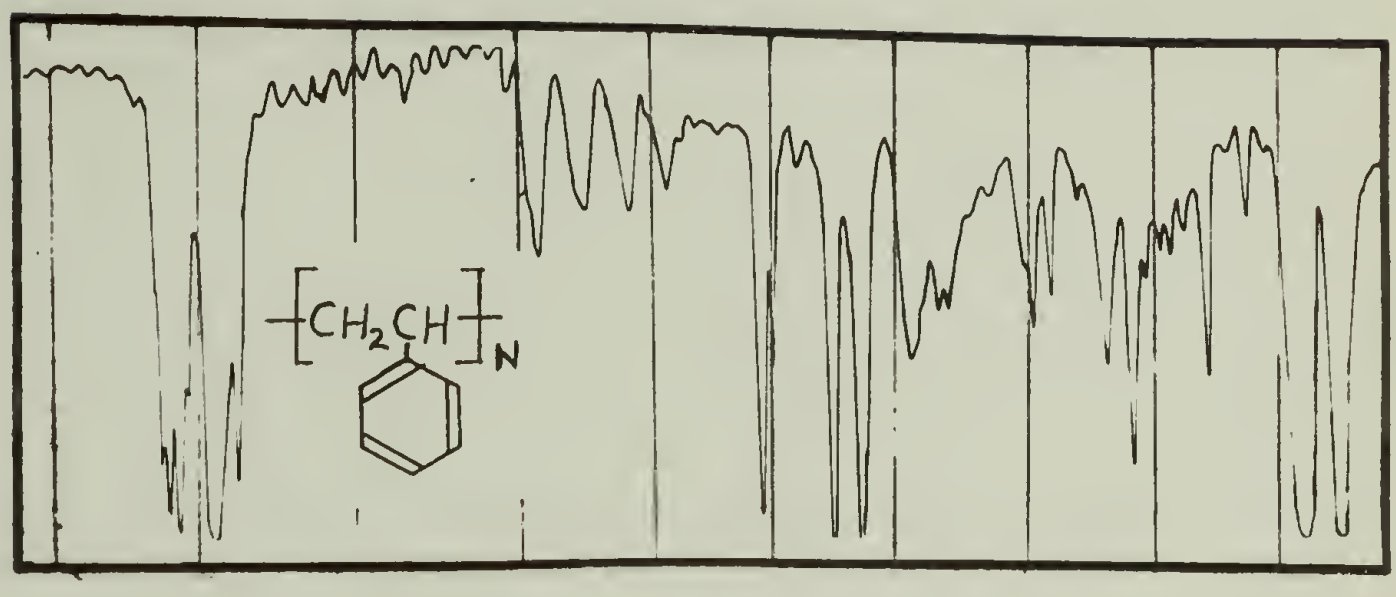
IR-20b. SBS-B-2 copolymer



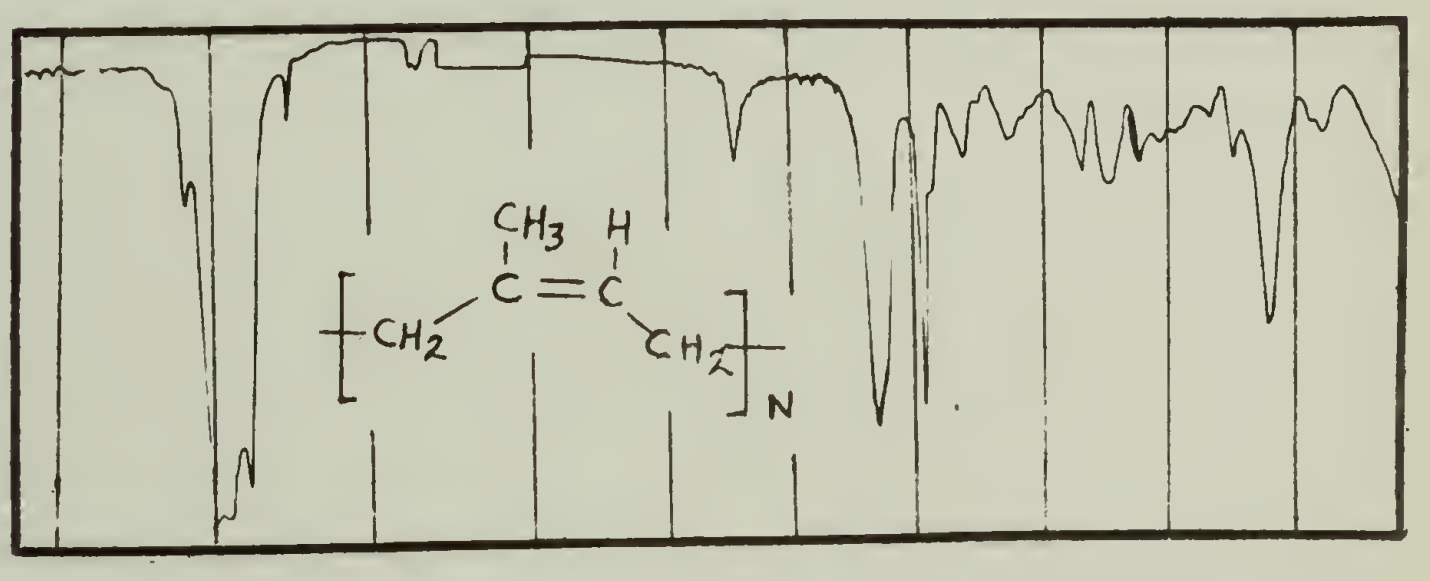
IR-20c. SBS-B-3 copolymer



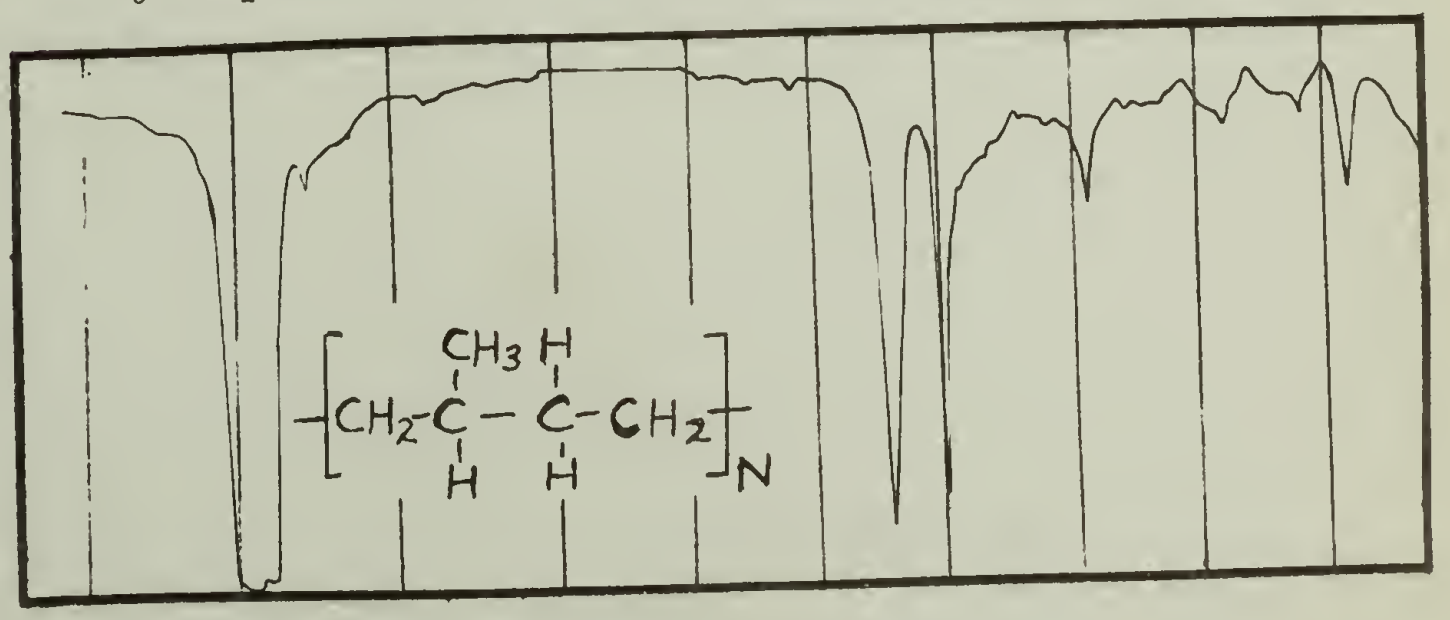
IR-21. Polystyrene



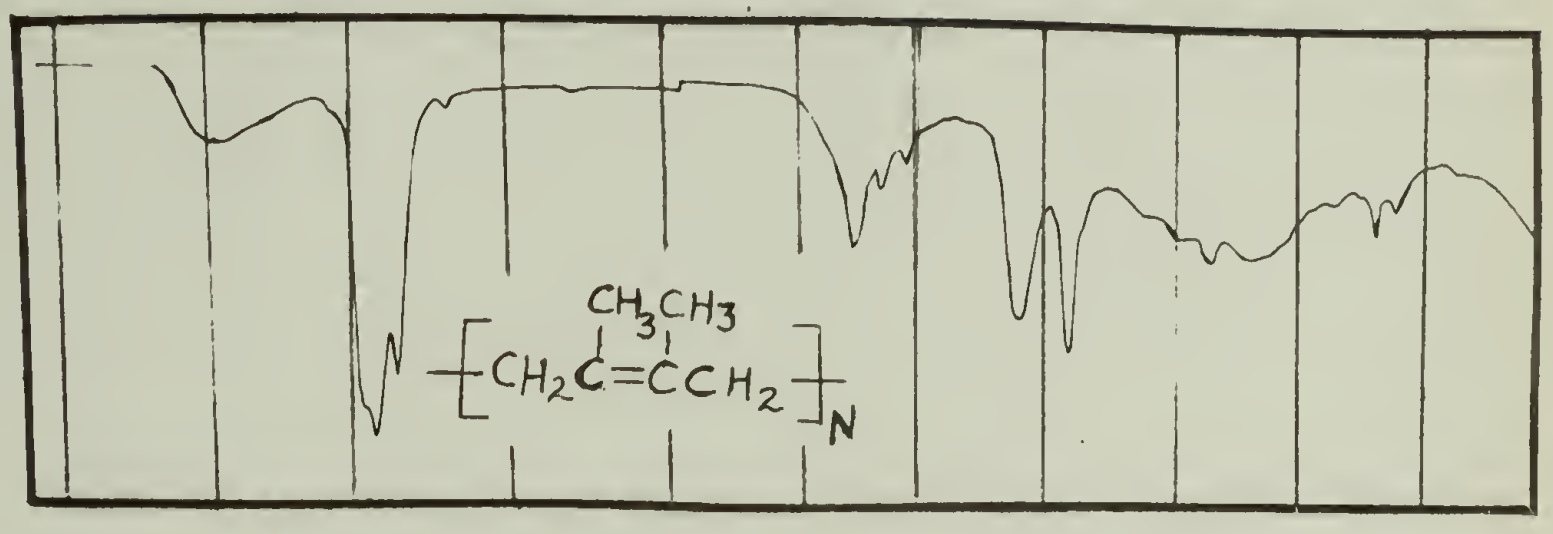
IR-22. Polyisoprene



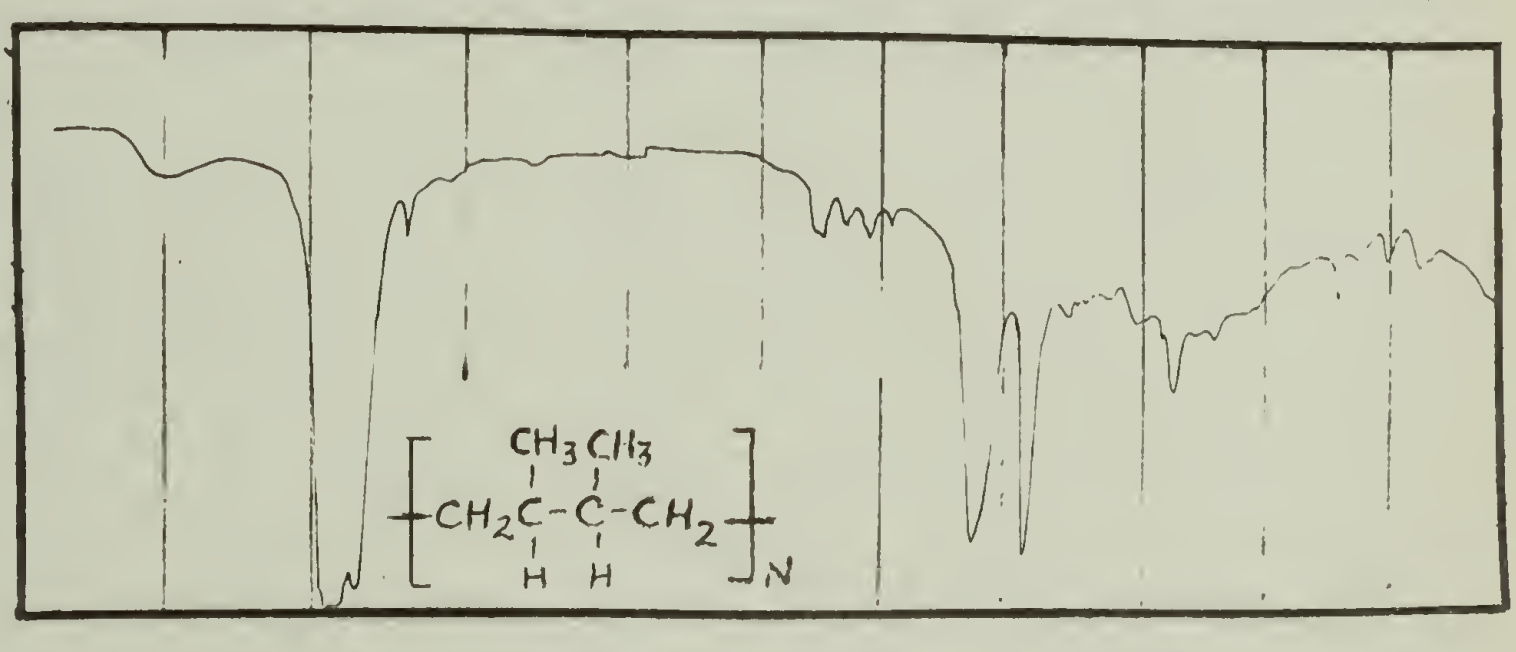
IR-23. Polyisoprene after diimide hydrogenation



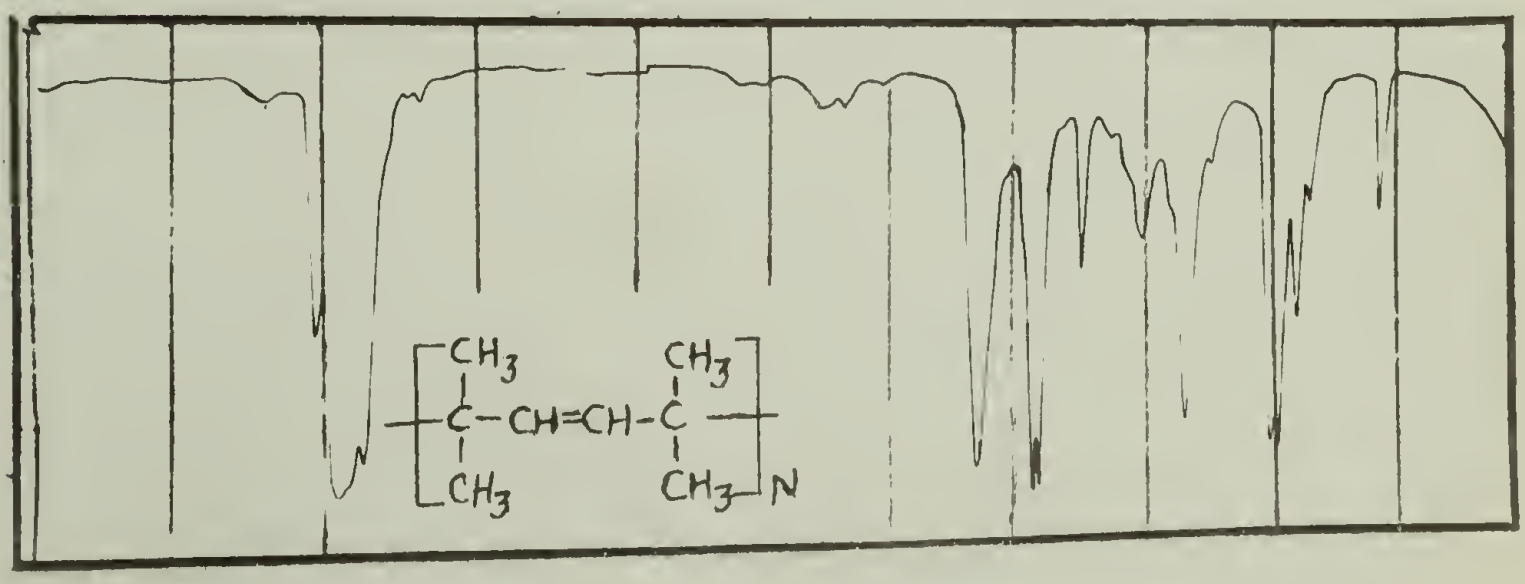
IR-24. poly(2,3-dimethylbutadiene)



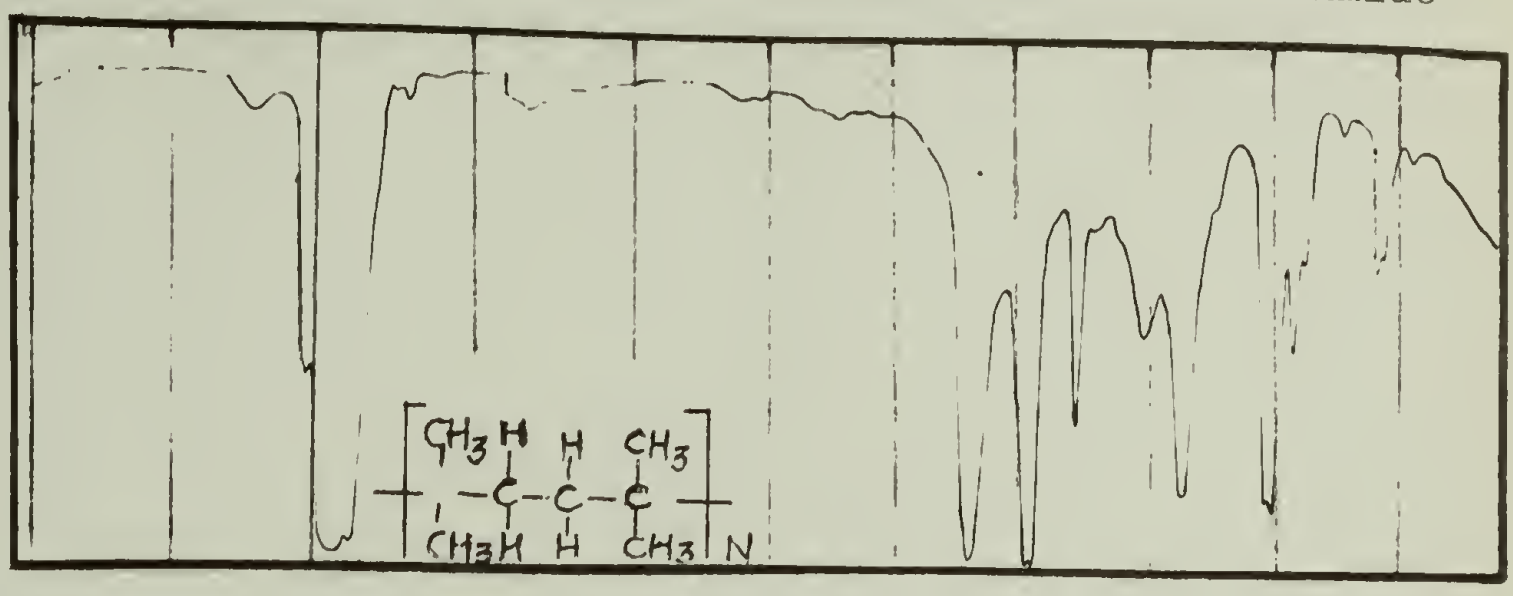
IR-25. Partially hydrogenated poly(2,3-dimethylbutadiene)



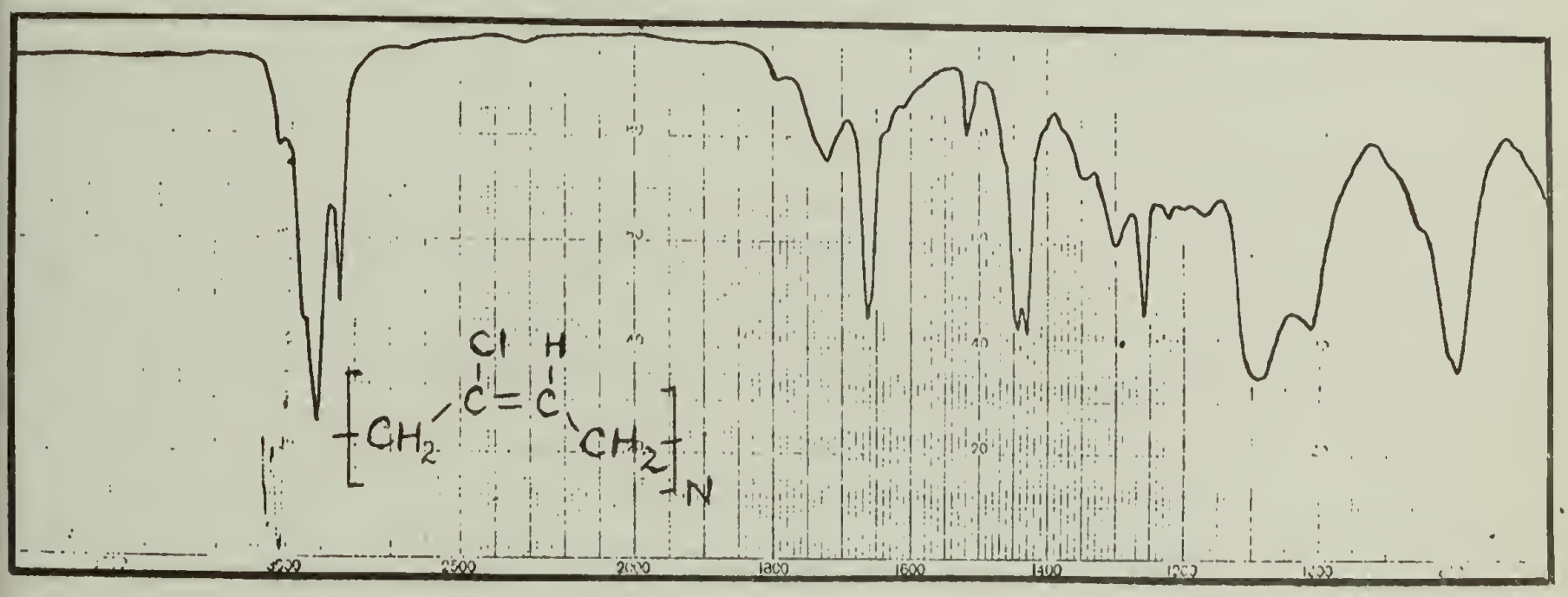
IR-26. Methyl rubber



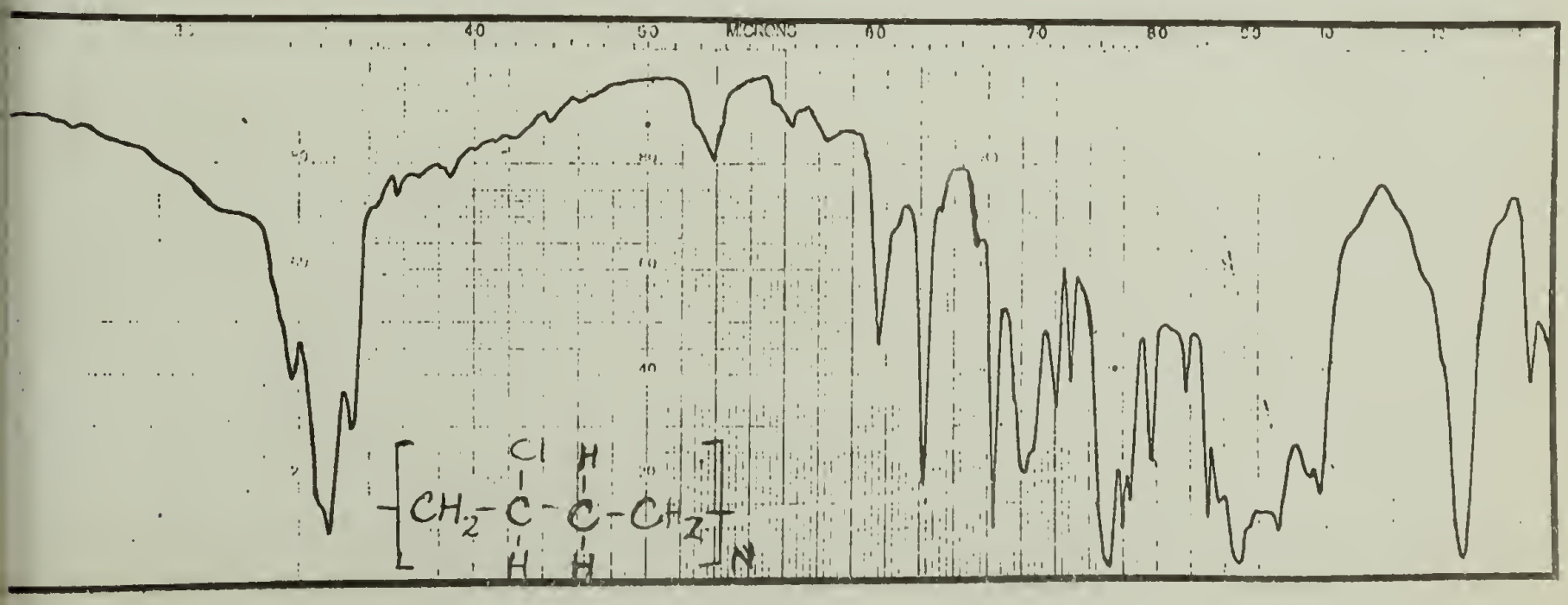
IR-27. Methyl rubber partially hydrogenated with diimide



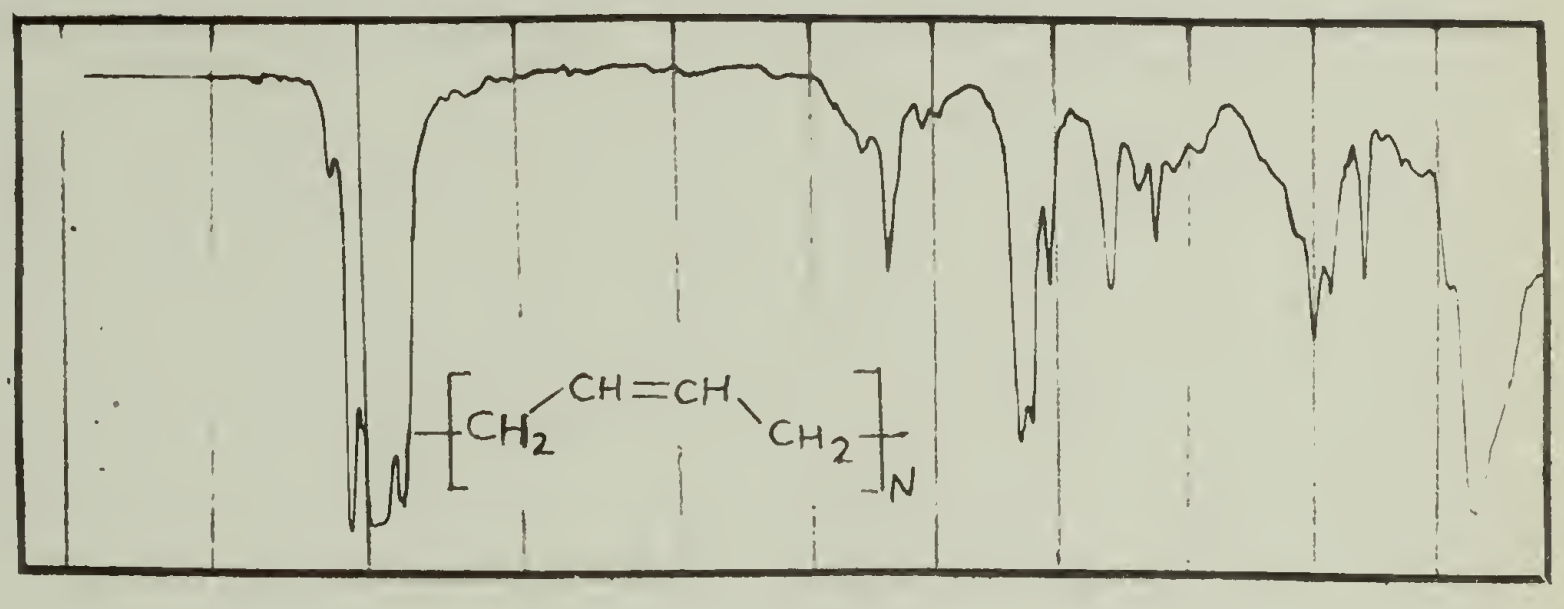
IR-28. Polychloroprene



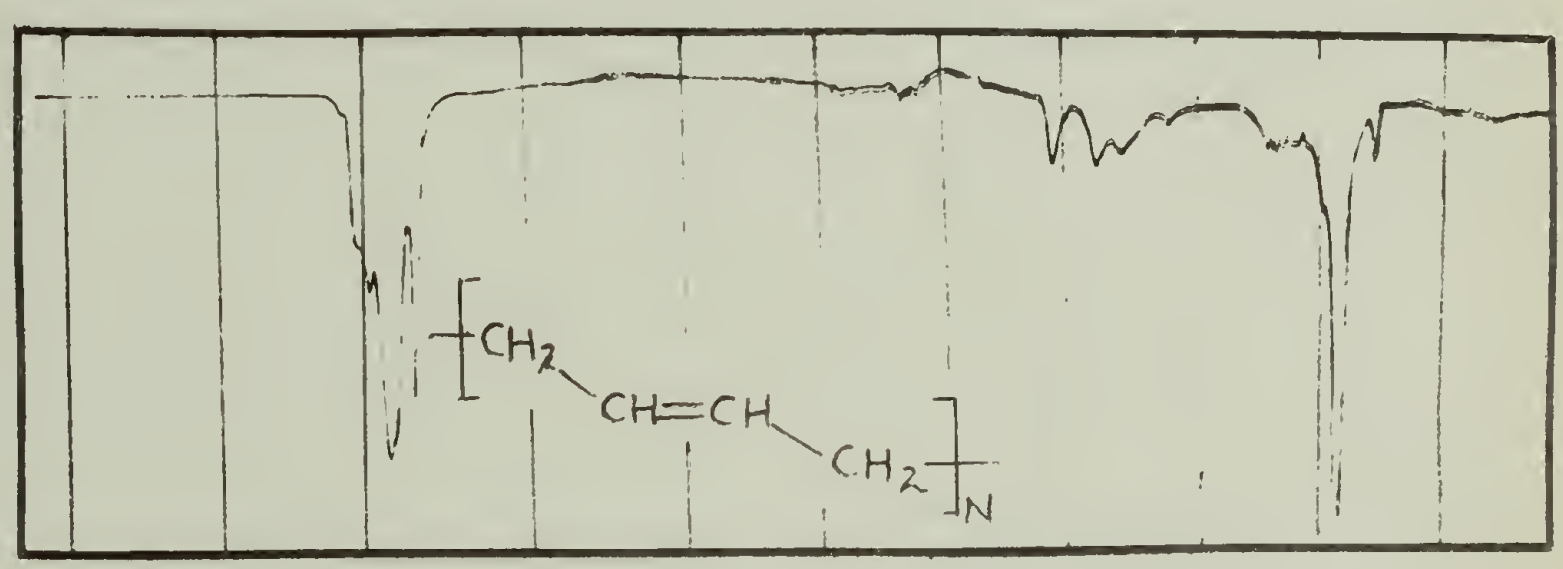
IR-29. Partially hydrogenated polychloroprene



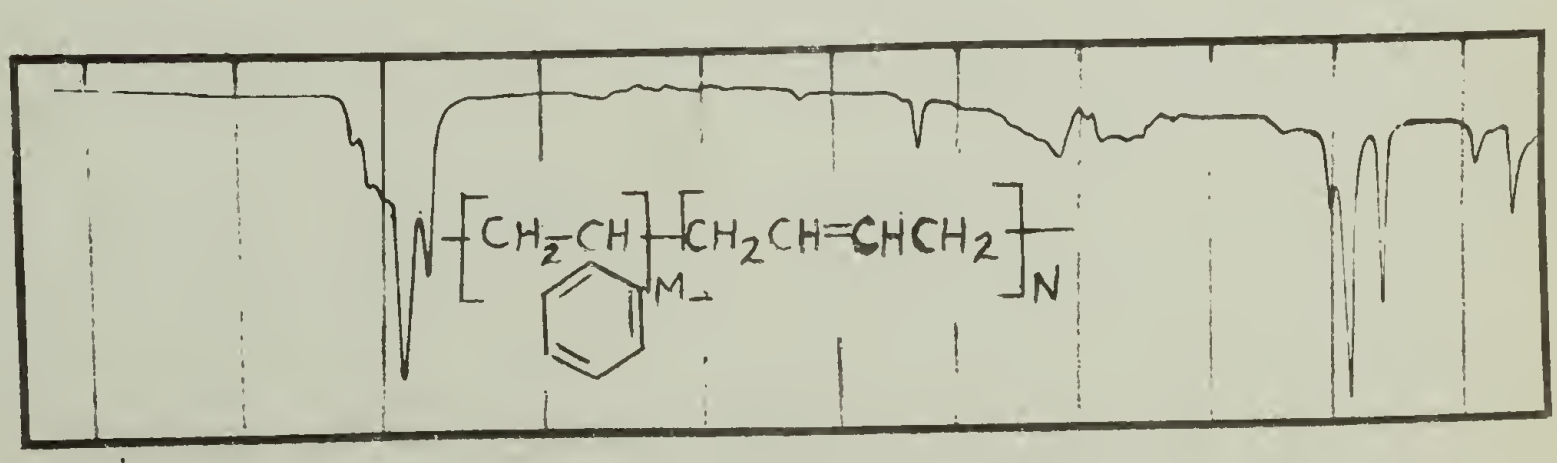
IR-30a. cis-1,4-Polybutadiene

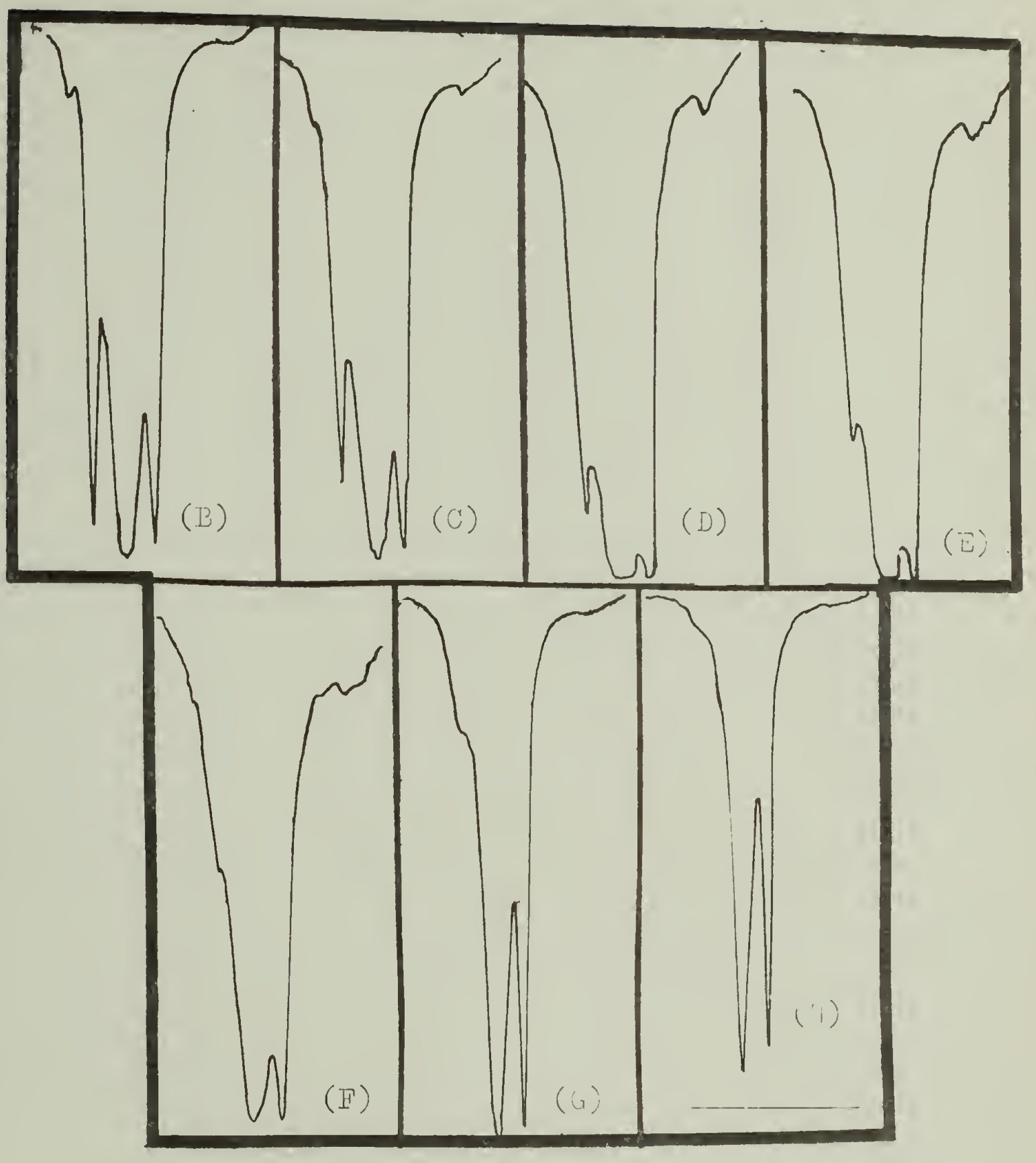


IR-31a. trans-1,4-Polybutadiene

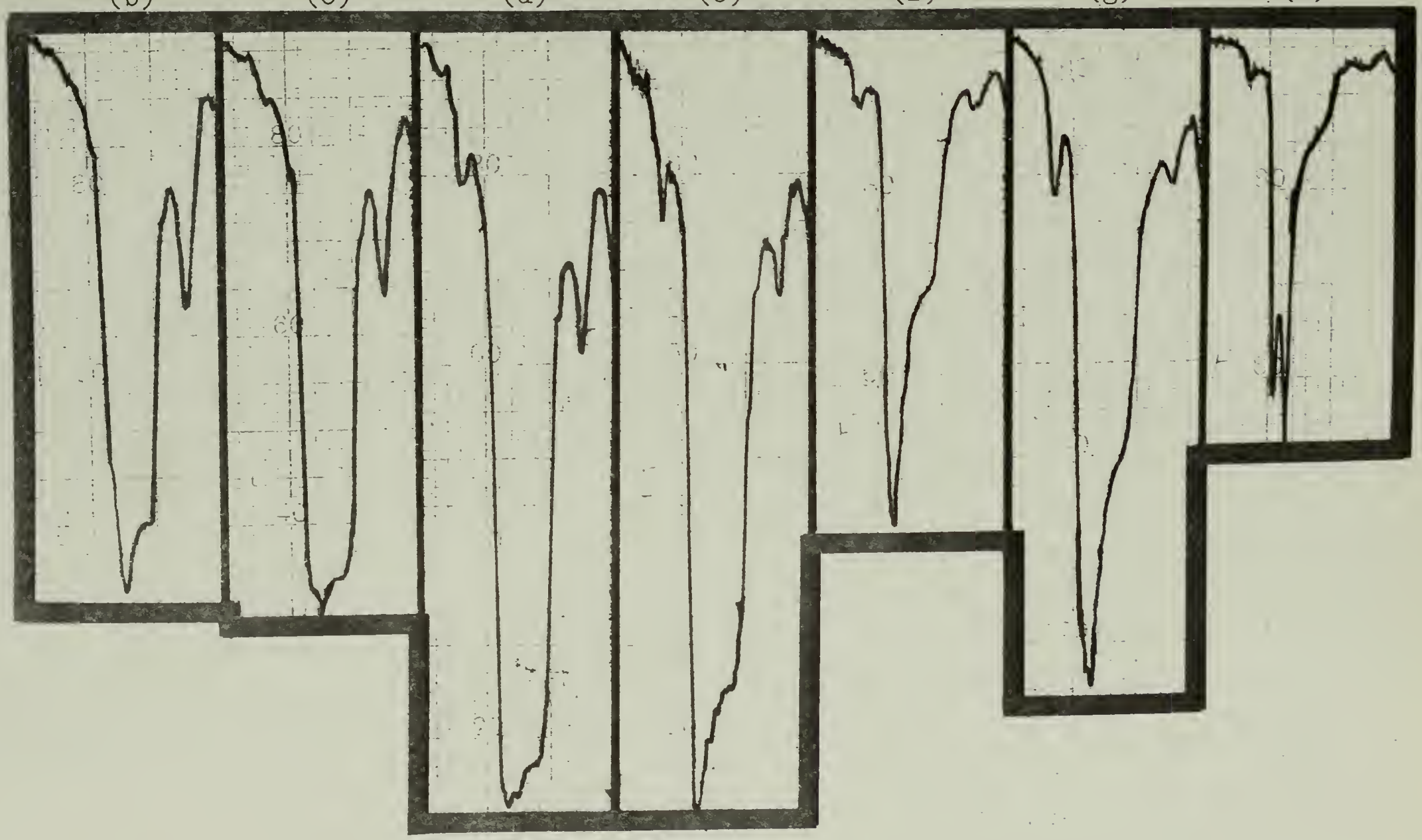


IR-32. Styrene-Butadiene random copolymer

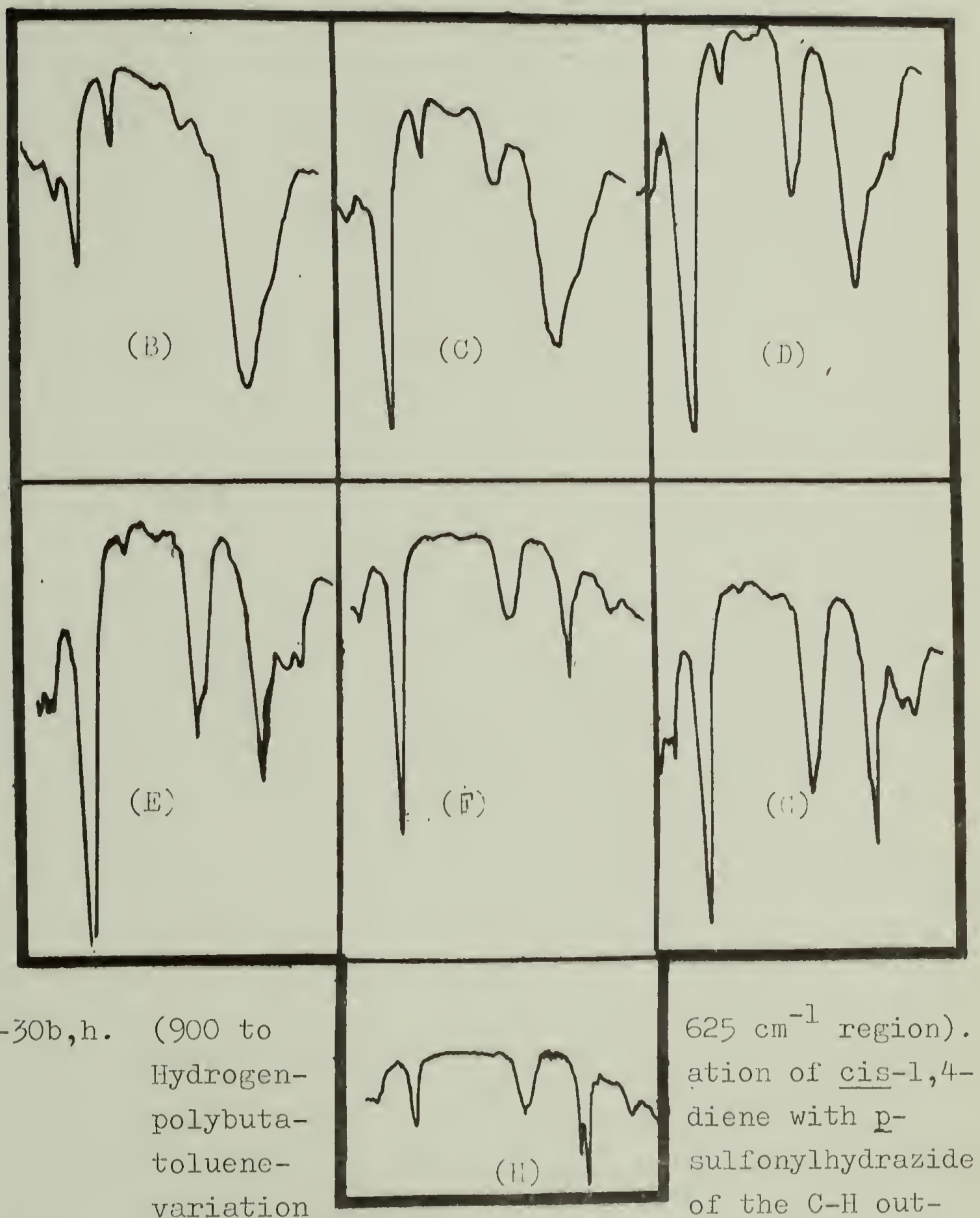




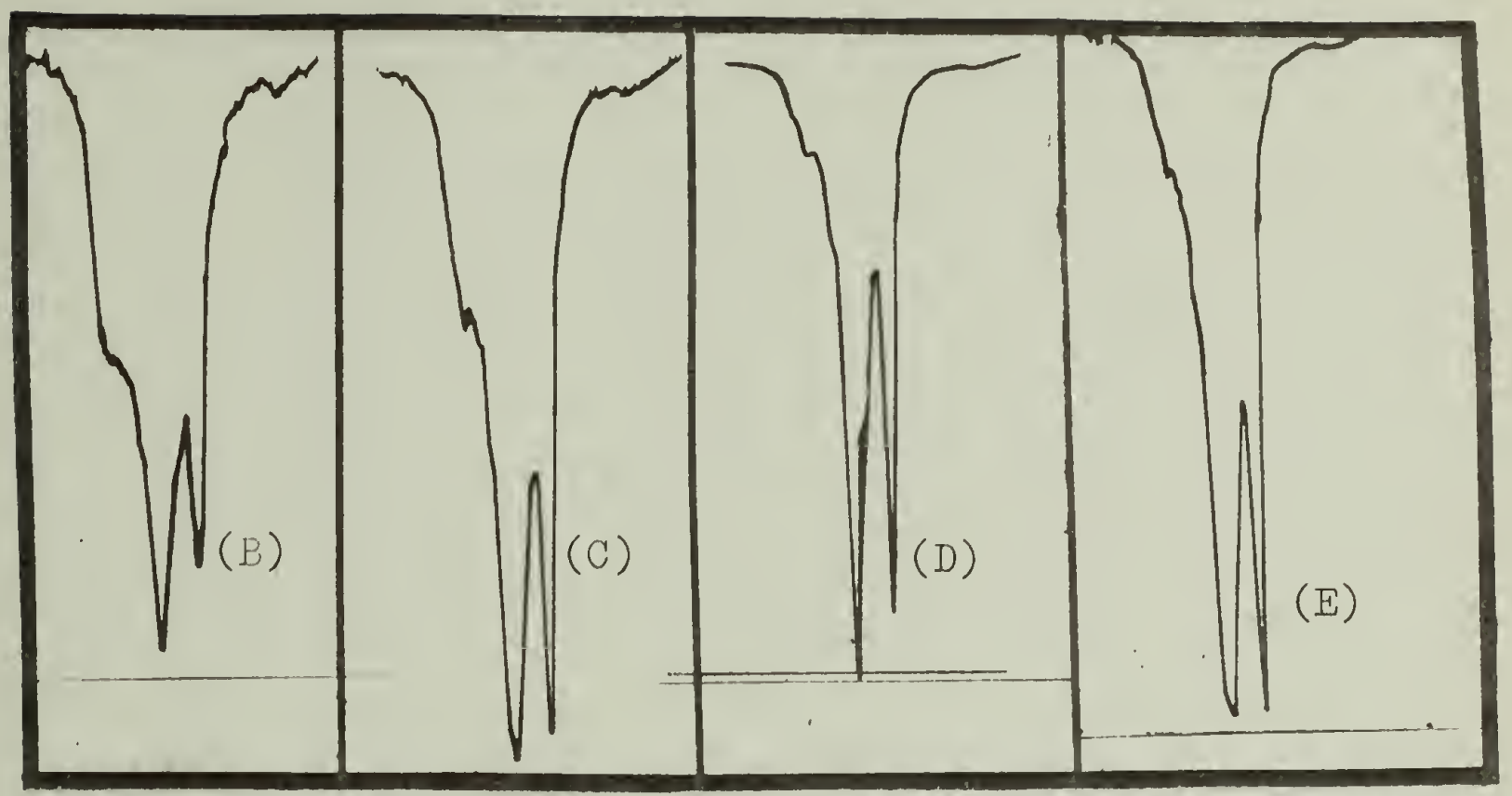
IR-30b,h. (3100 to 2800 cm^{-1} region). Hydrogenation of cis-1,4-polybutadiene with p-toluenesulfonyl-hydrazide; variation of C-H stretching bands in the 2800 to 3100 cm^{-1} region as a function of reaction time.

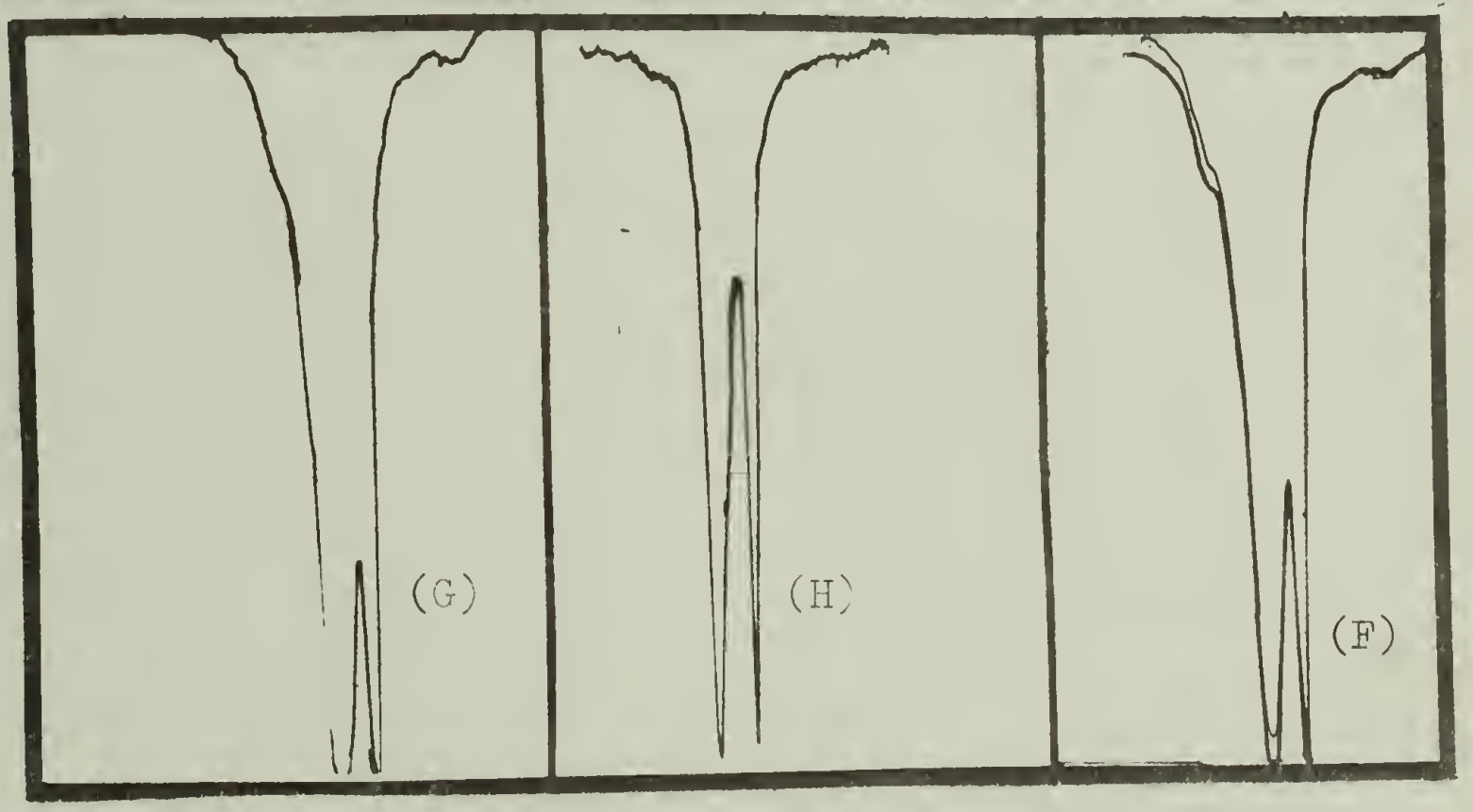


IR-30b,h. (1550 to 1400 cm^{-1} region). Hydrogenation of cis-1,4-polybutadiene with p-toluenesulfonylhydrazide; variation of CH_2 deformation bands in the region 1400 to 1550 cm^{-1} as a function of reaction time.



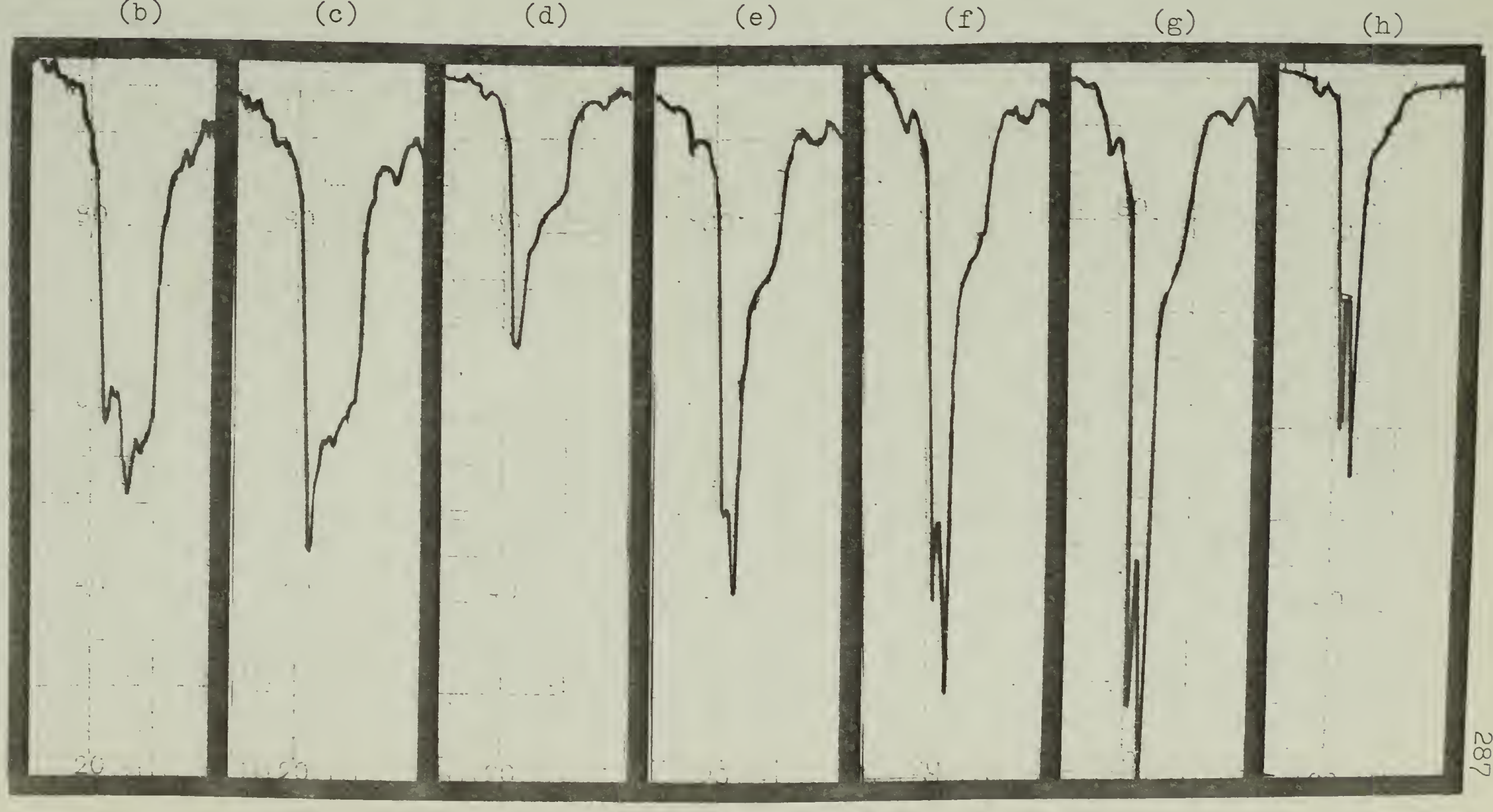
IR-30b,h. (900 to 625 cm^{-1} region). Hydrogenation of cis-1,4-polybutadiene with p-toluenesulfonylhydrazide; variation of the C-H out-of-plane stretching bands in the region 625 to 900 cm^{-1} as a function of reaction time.

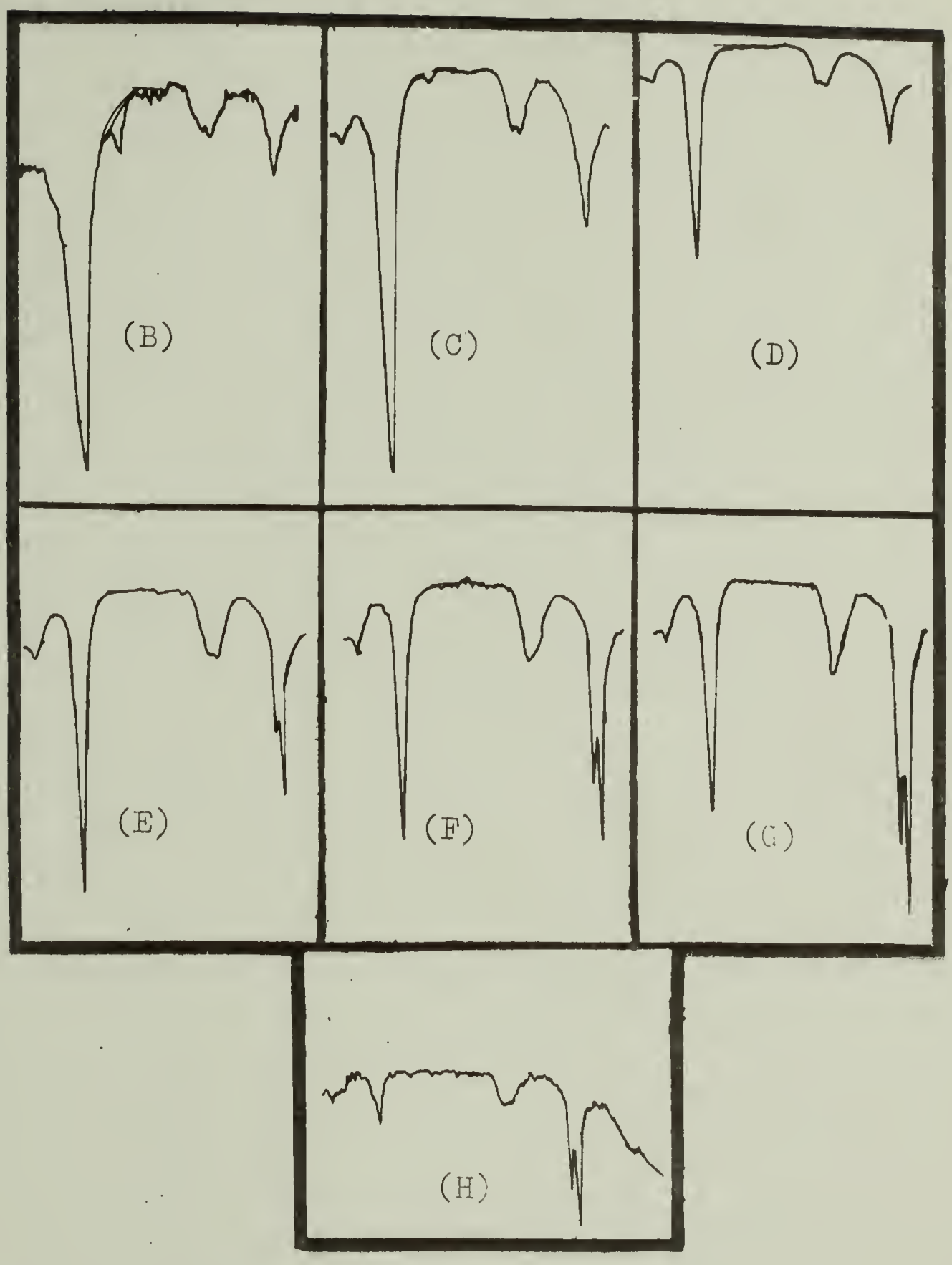




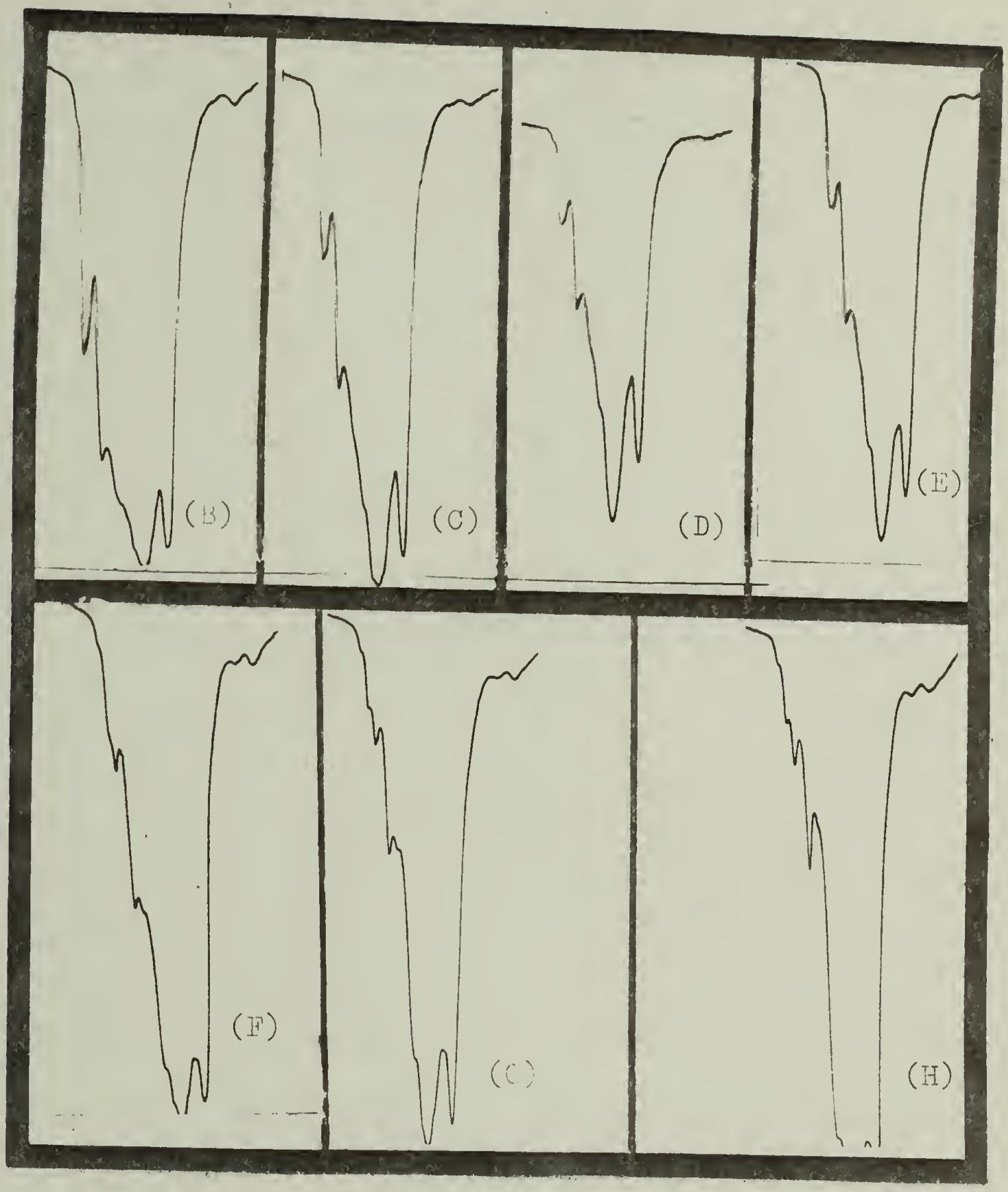
IR-31b,h. (3100 to 2800 cm^{-1} region). Hydrogenation of trans-1,4-polybutadiene with p-toluenesulfonyl-hydrazide; variation of the C-H stretching bands in the 3100 to 2800 cm^{-1} region as a function of reaction time.

IR-31b,h. (1550 to 1400 cm^{-1} region). Hydrogenation of <u>trans</u>-1,4-polybutadiene with <u>p</u>-toluenesulfonylhydrazide; variation of C-H deformation bands in the region 1550 to 1400 cm^{-1} as a function of reaction time.

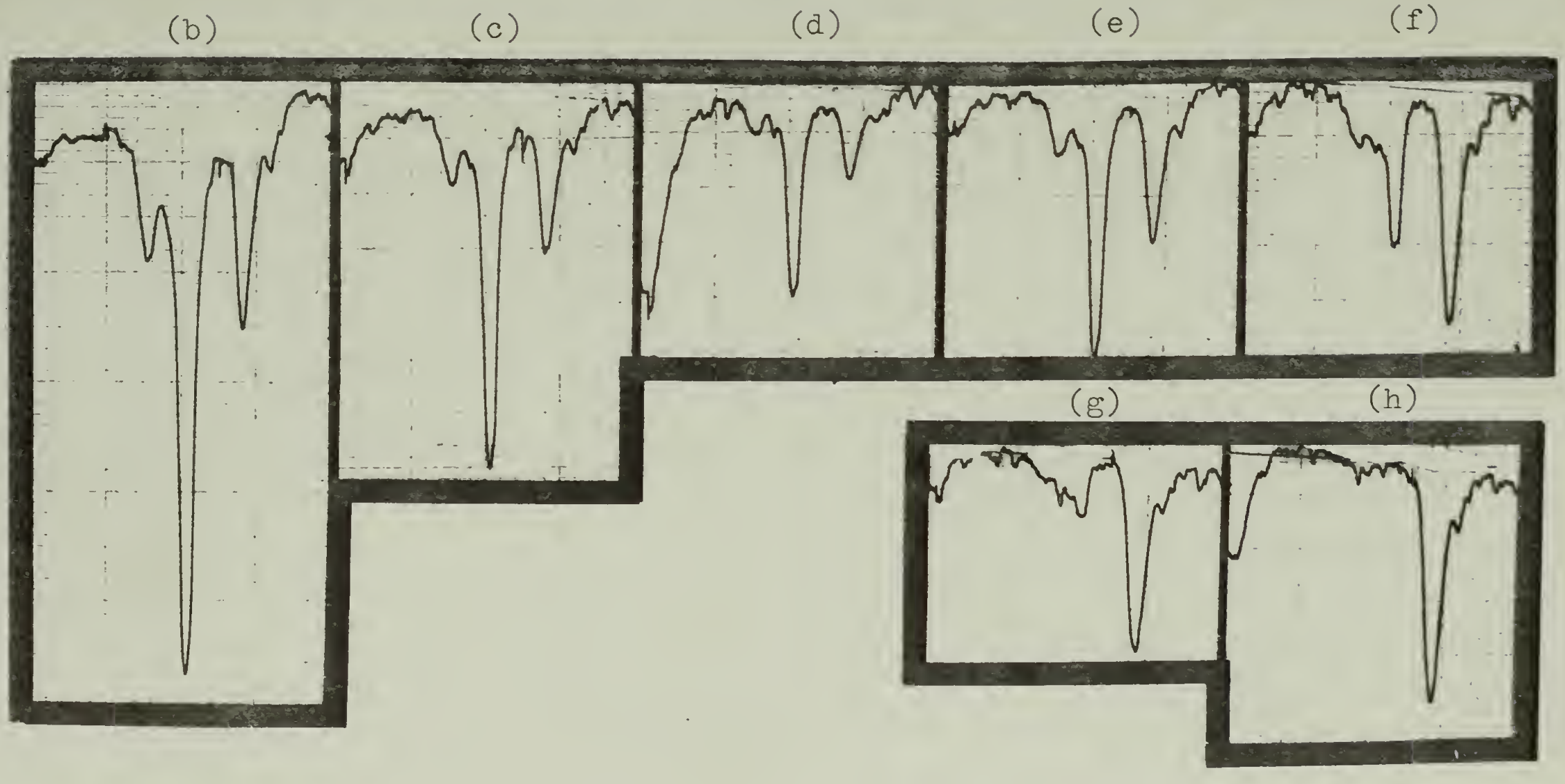




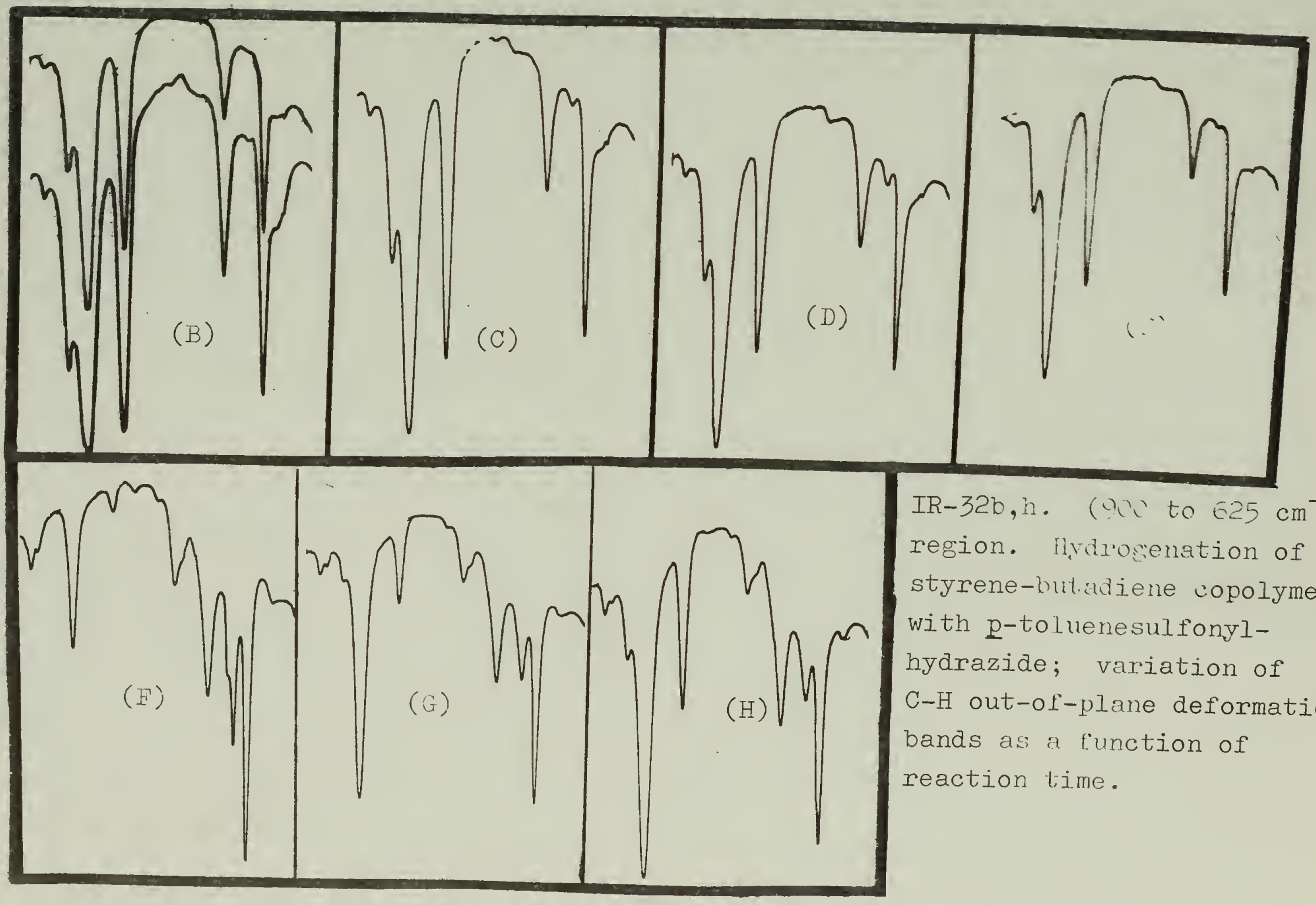
IR-31b,h. (900 to 625 cm^{-1} region). Hydrogenation of trans-1,4-polybutadiene with p-toluenesulfonyl-hydrazide; variation of C-H out-of-plane deformation bands in the region 900 to 625 cm^{-1} as a function of reaction time.



IR-32b,h. (3100 to 2800 cm^{-1} region). Hydrogenation of styrene-butadiene random copolymer with p-toluenesulvonylhydrazide; variation of the C-H stretching bands in the region 3100 to 2800 cm^{-1} as a function of reaction time.



IR-32b,h. (1550 to 1400 cm^{-1} region). Hydrogenation of styrene-butadiene random copolymer with p-toluenesulfonylhydrazide; variation of vinyl C=C stretching band as a function of reaction time.

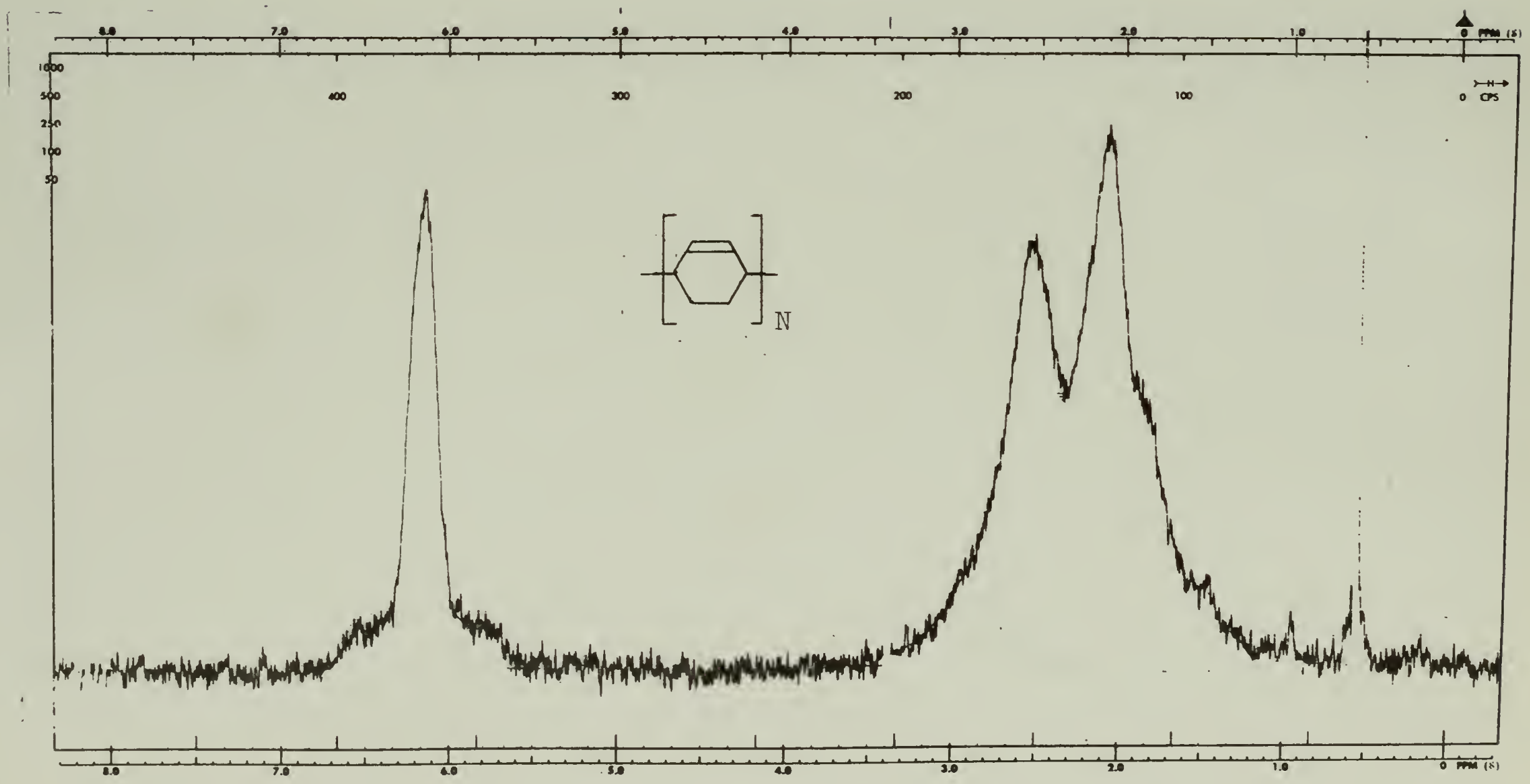


IR-32b,h. (900 to 625 cm^{-1} region. Hydrogenation of styrene-butadiene copolymer with p-toluenesulfonyl-hydrazide; variation of C-H out-of-plane deformation bands as a function of reaction time.

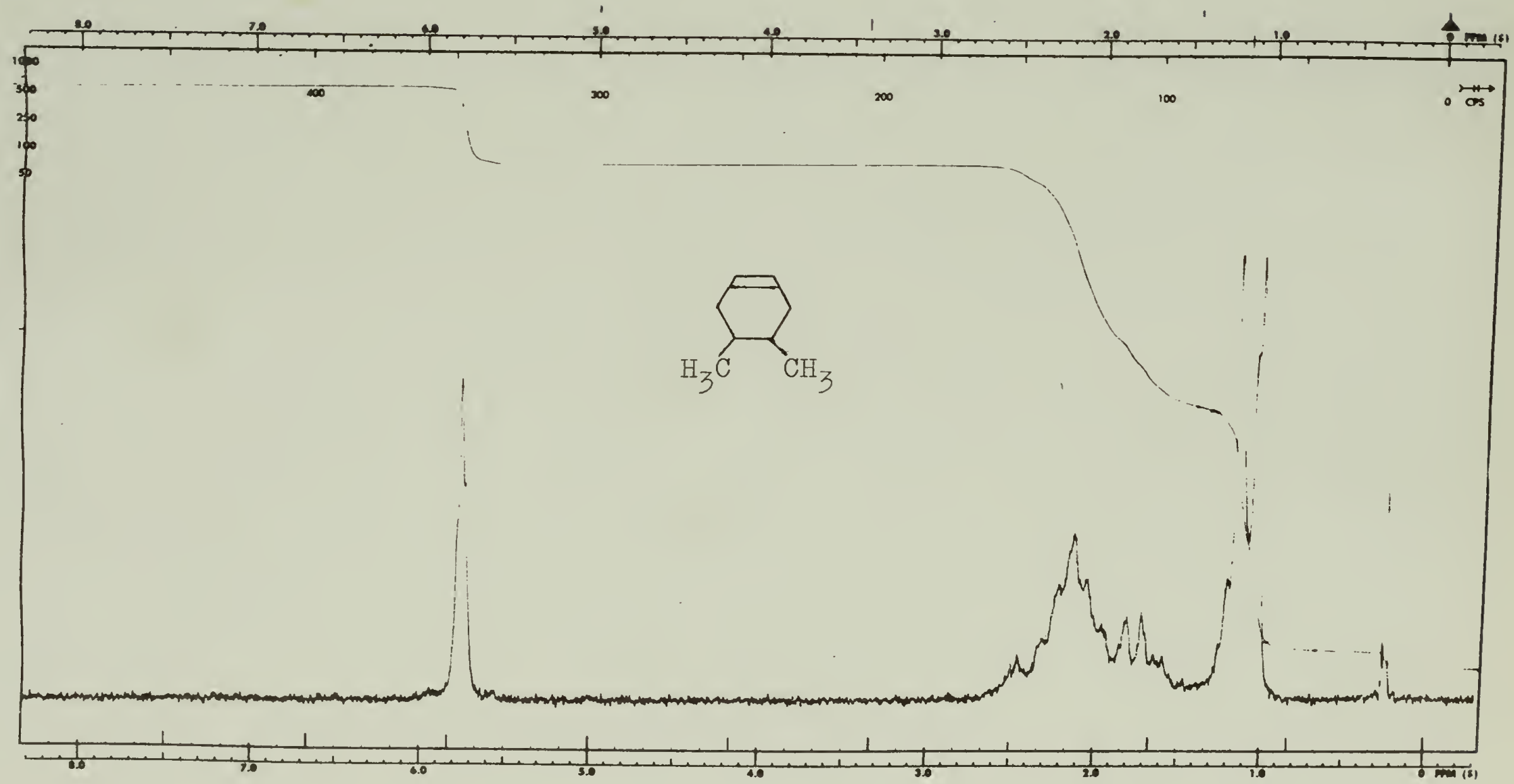
APPENDIX 4

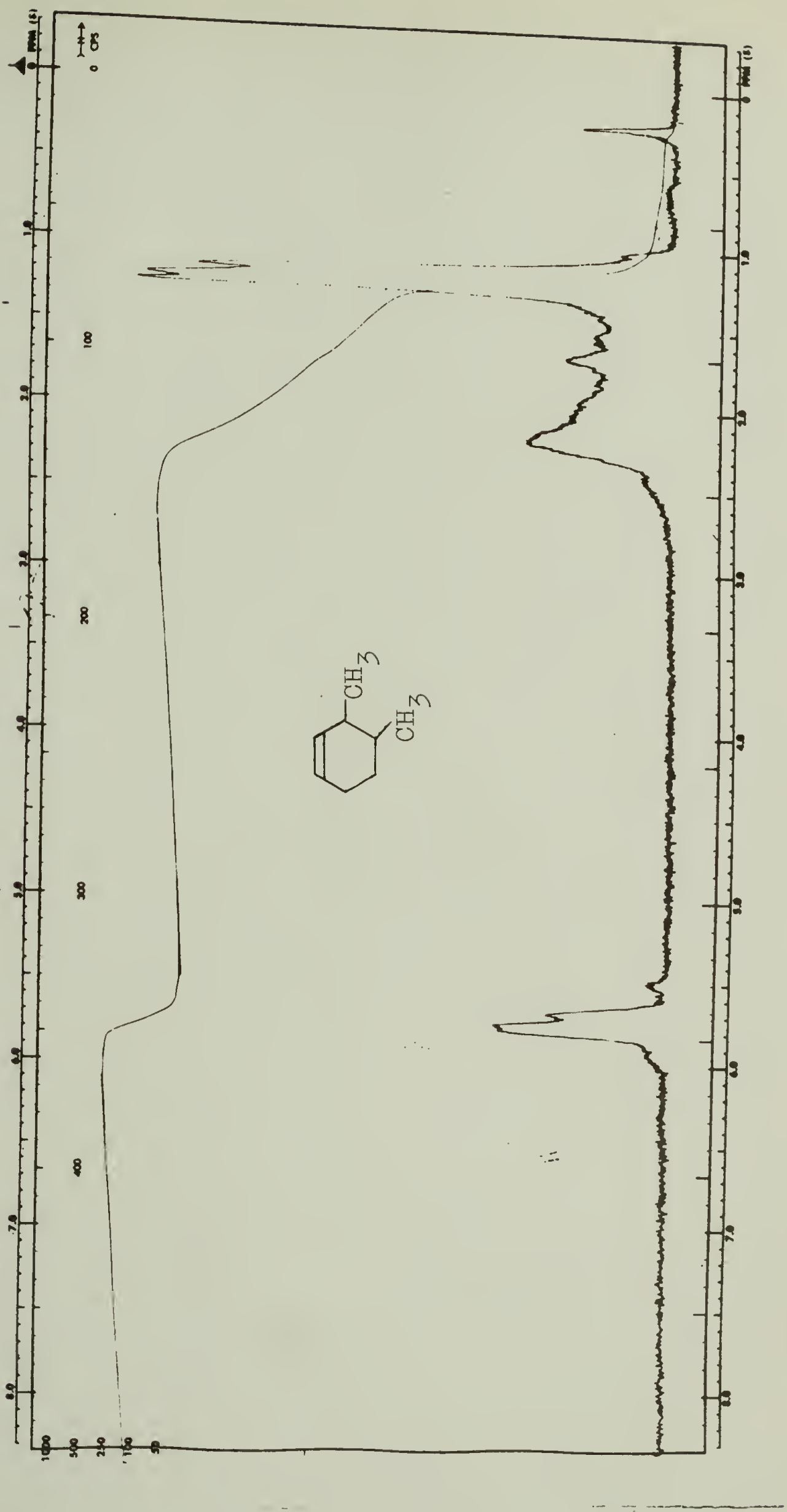
NUCLEAR MAGNETIC RESONANCE SPECTRA

NMR-1. Polycyclohexadiene (P-50-1)



NMR-2. 4,5-dimethylcyclohexene





NMR-3. 3,4-dimethylcyclohexene

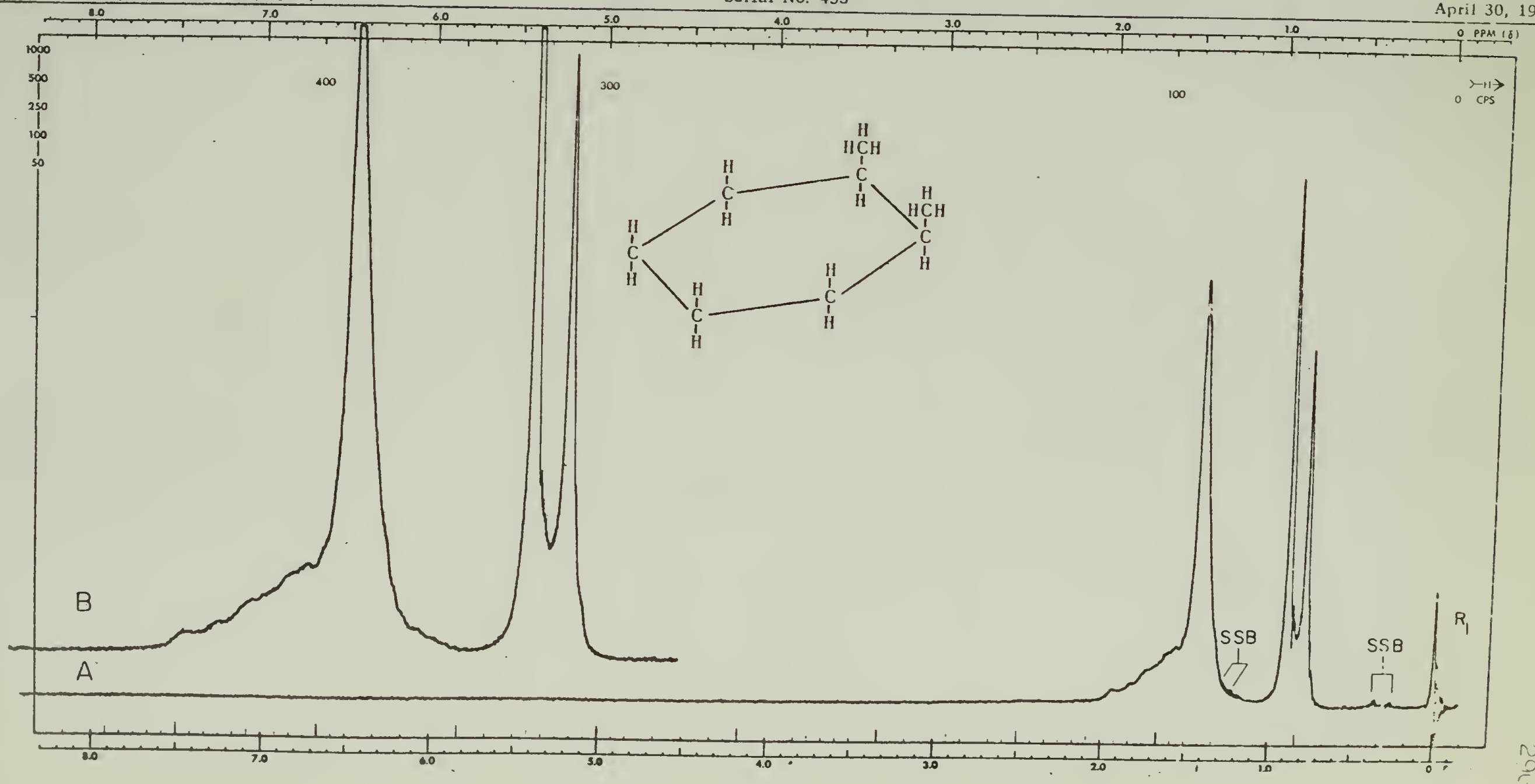
NMR-4. cis-1,2-dimethylcyclohexane

Contributed by the Texas A&M University, Department of Chemistry, College Station, Texas

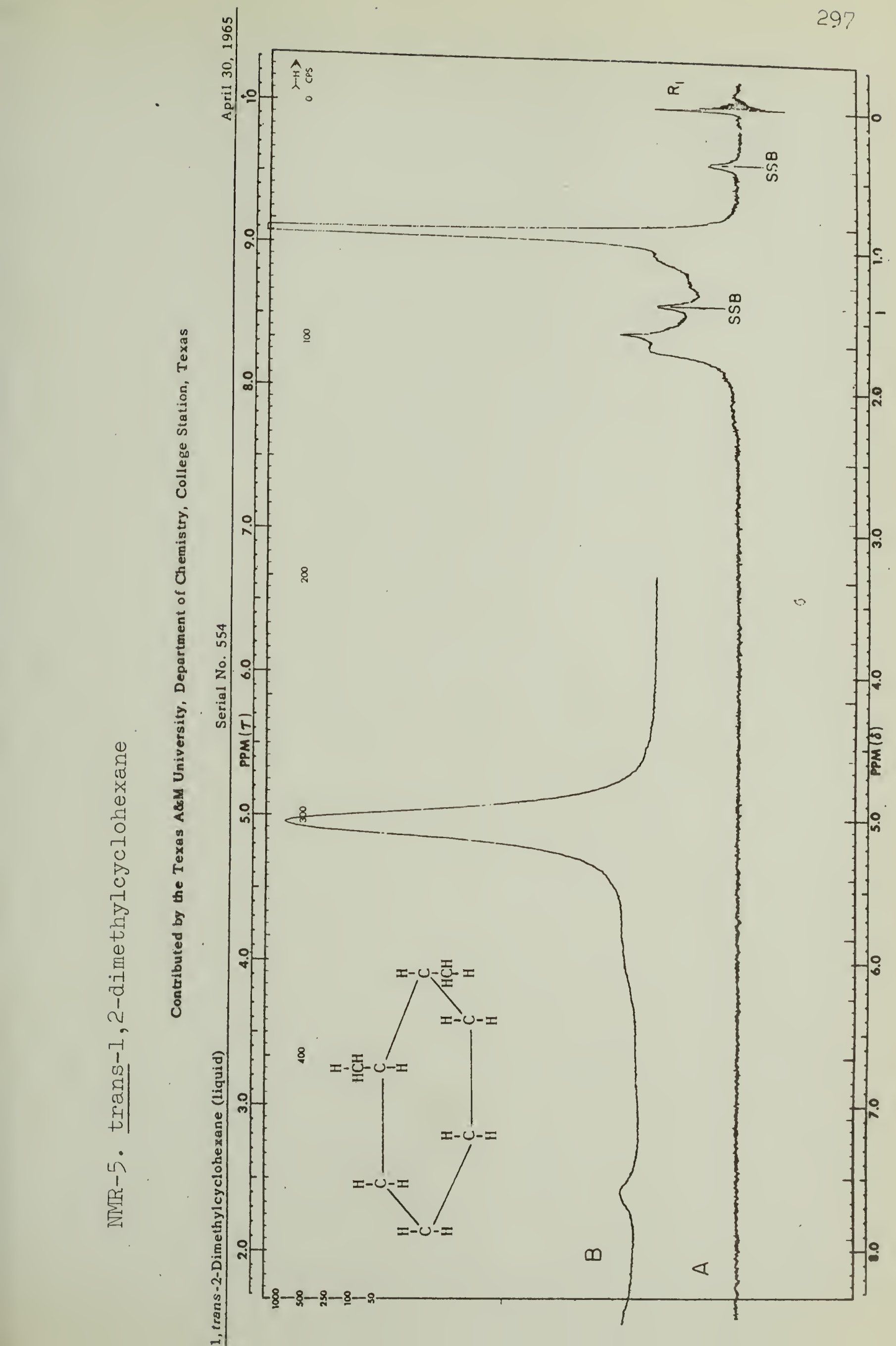
1,*cis*-2-Dimethylcyclohexane (liquid)

Serial No. 453

April 30, 1964



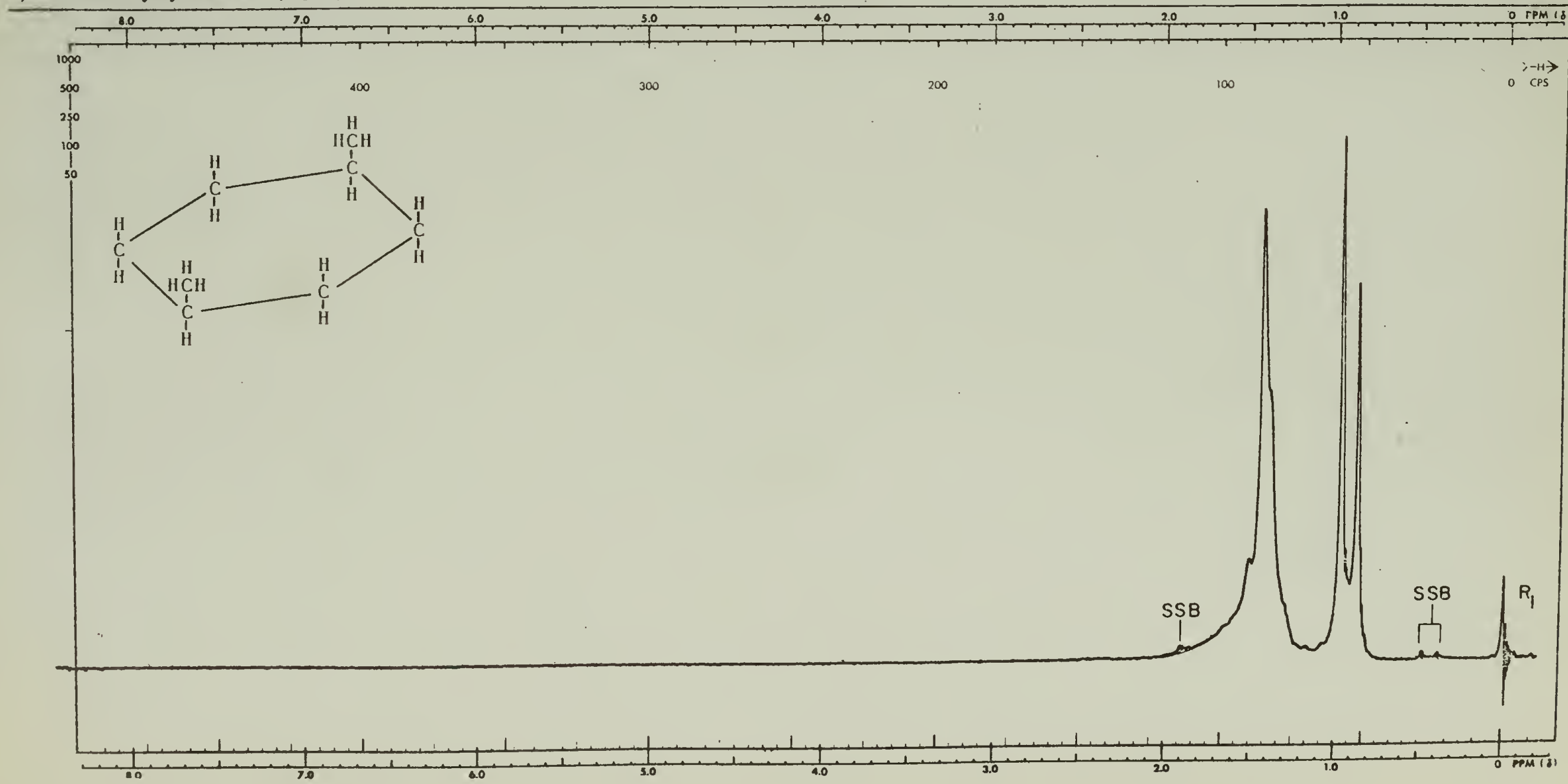
NMR-5. trans-1,2-dimethylcyclohexane



NMR-6. cis-1,4-dimethylcyclohexane

Contributed by the Texas A&M University, Department of Chemistry, College Station, Texas

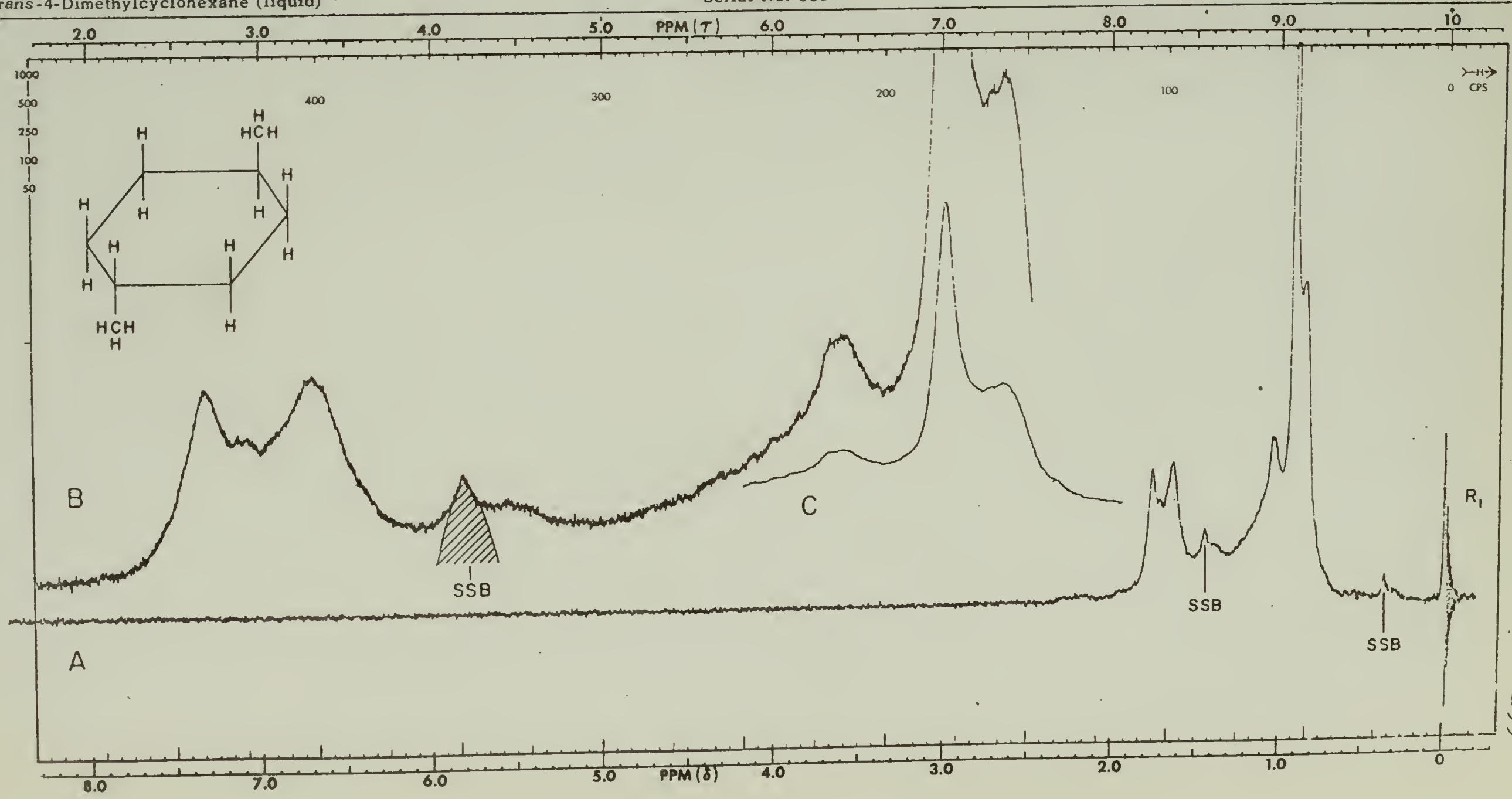
1,*cis*-4-Dimethylcyclohexane (liquid) Serial No. 455 April 30, 1964



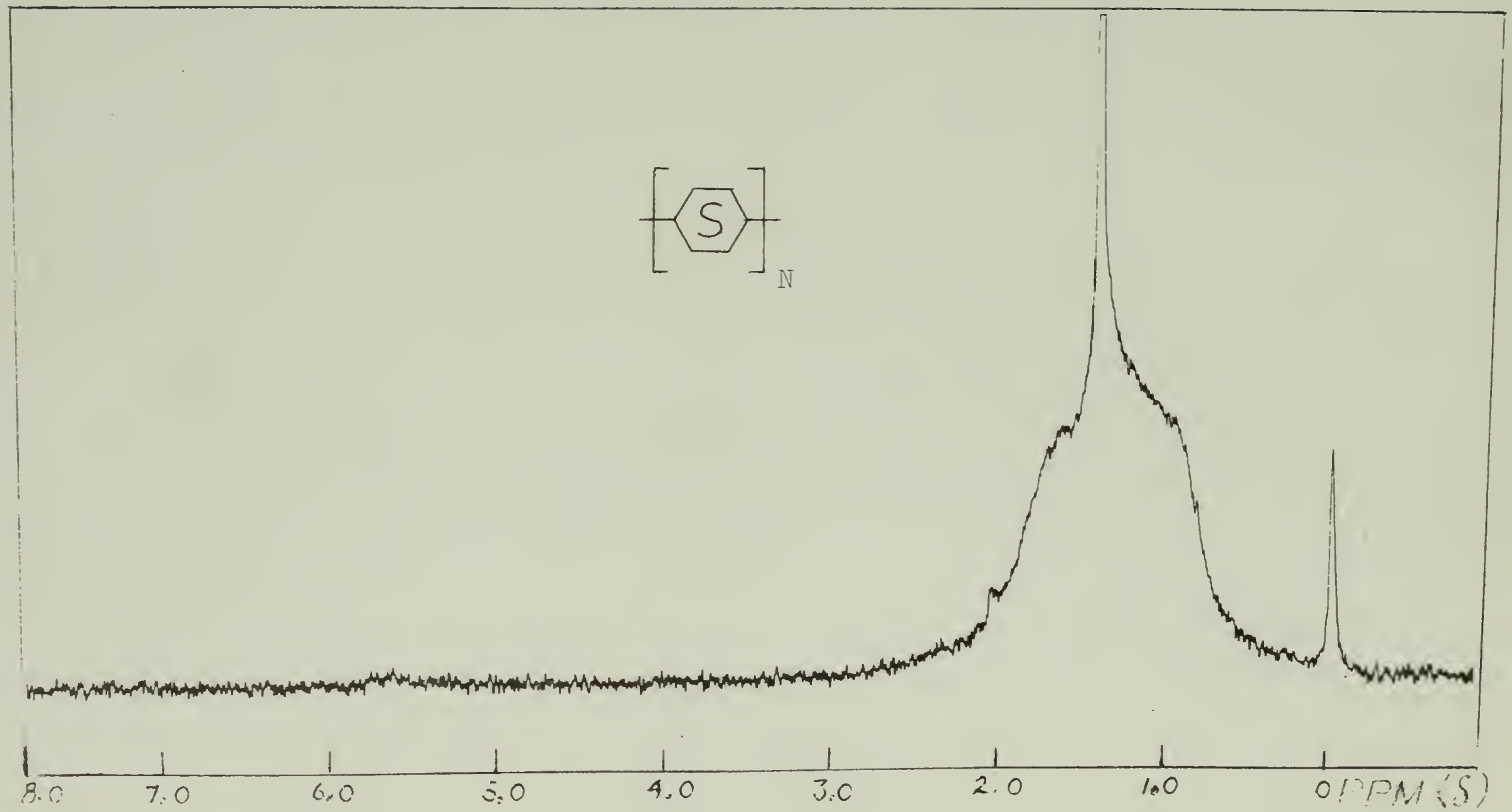
NMR-7. trans-1,4-dimethylcyclohexane

Contributed by the Texas A&M University, Department of Chemistry, College Station, Texas

1, *trans*-4-Dimethylcyclohexane (liquid) Serial No. 556 April 30, 1965

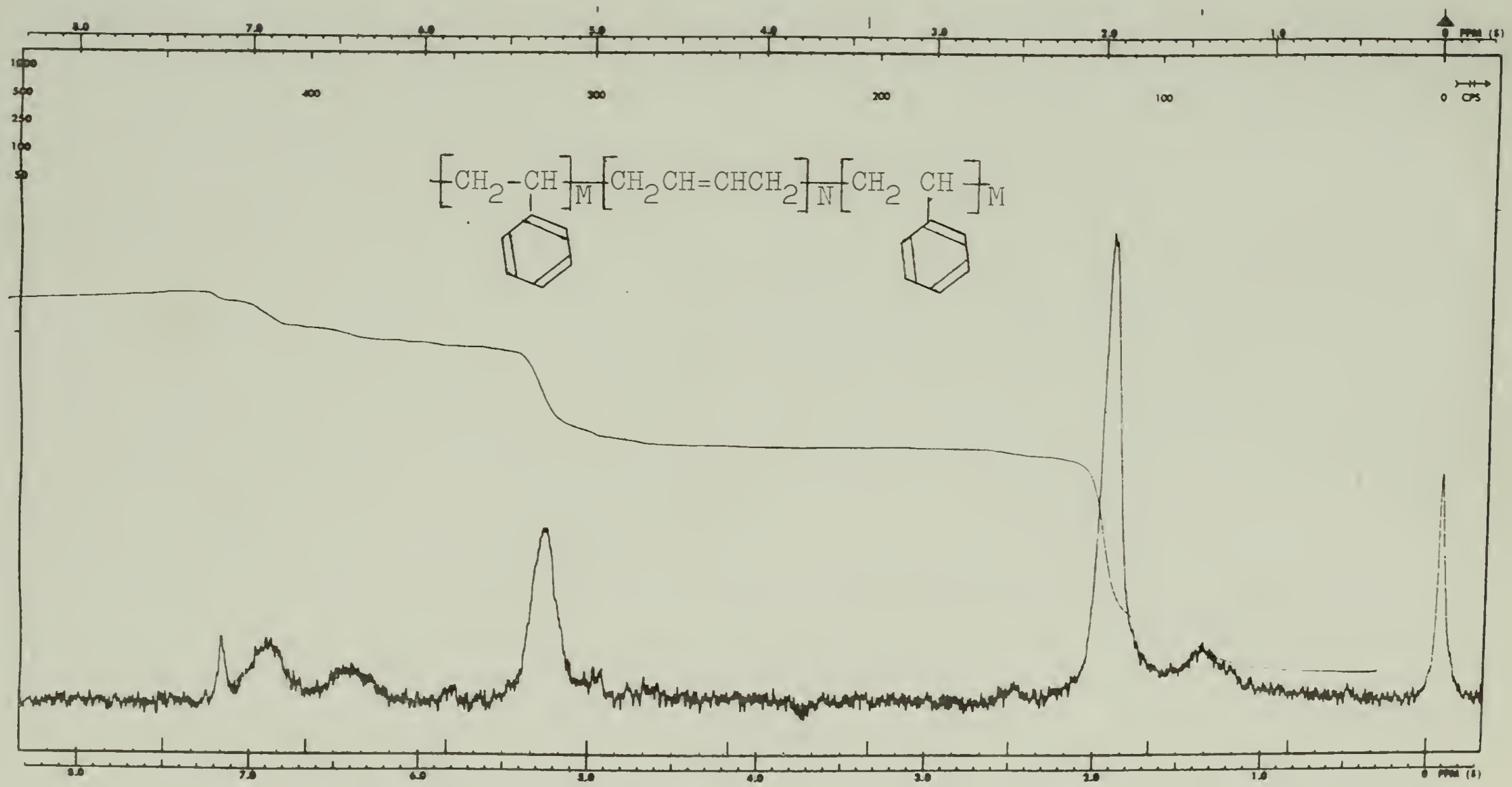


NMR-8. Polycyclohexane

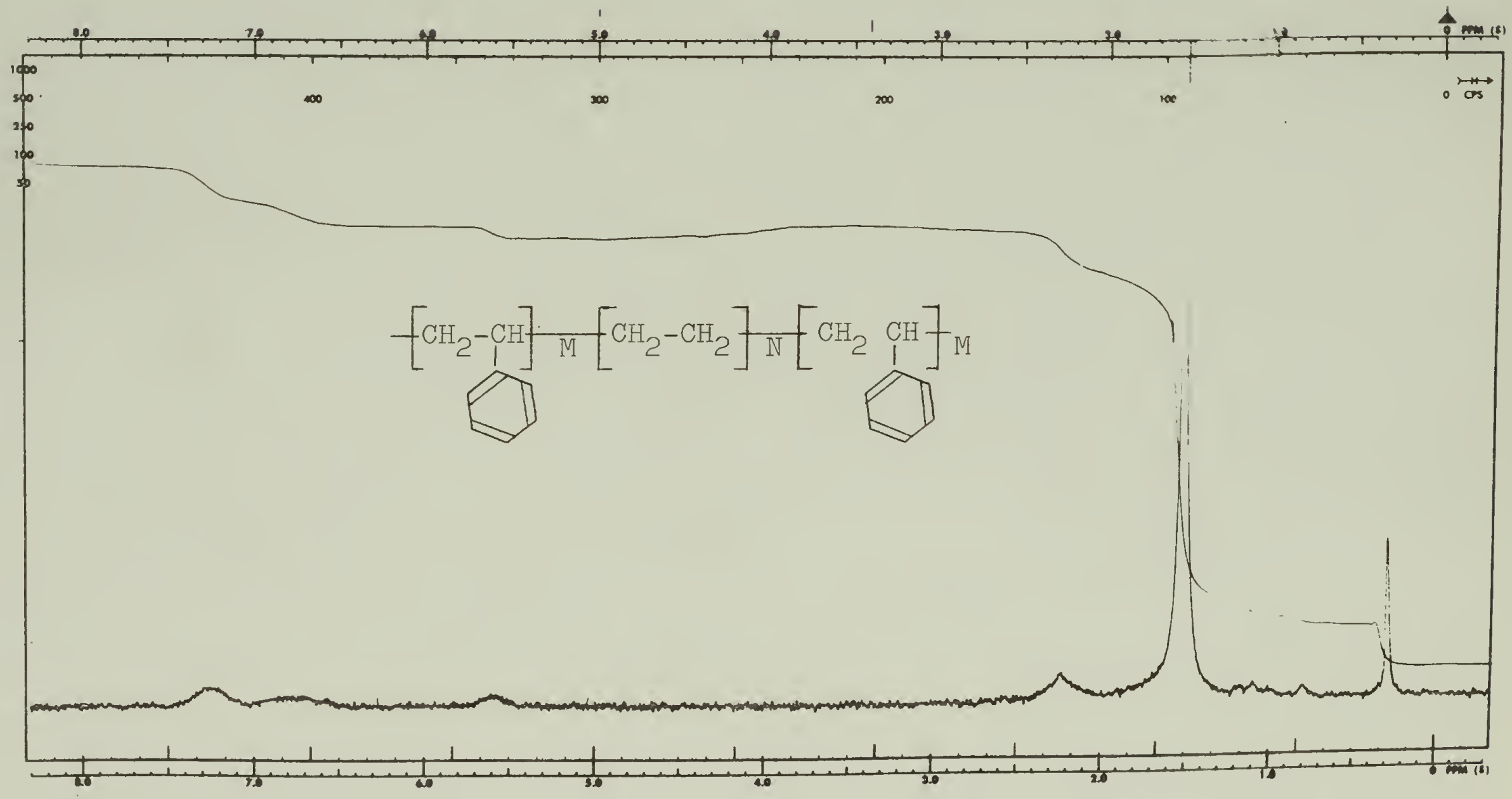


500

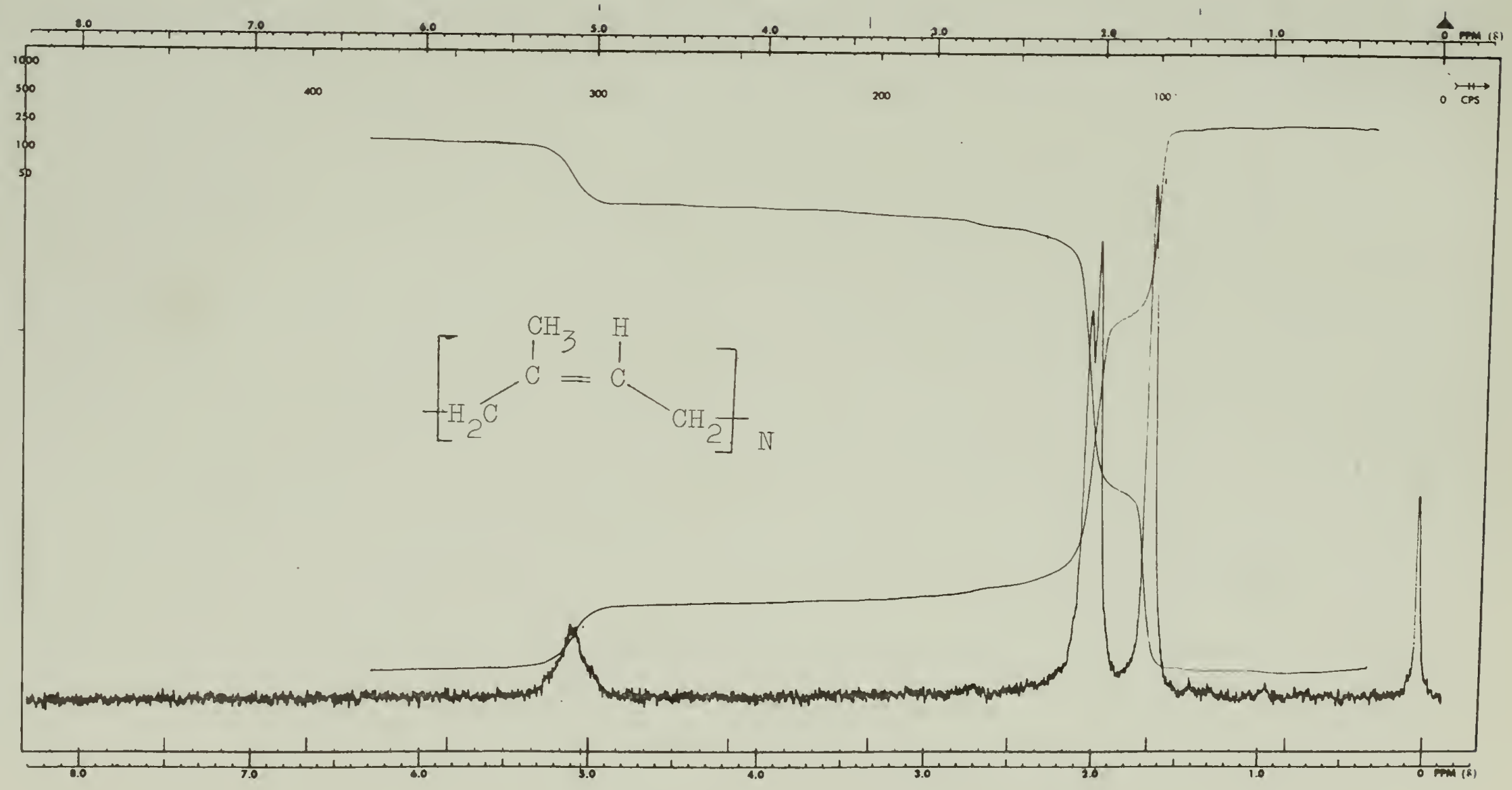
NMR-9. SBS 1 Copolymer



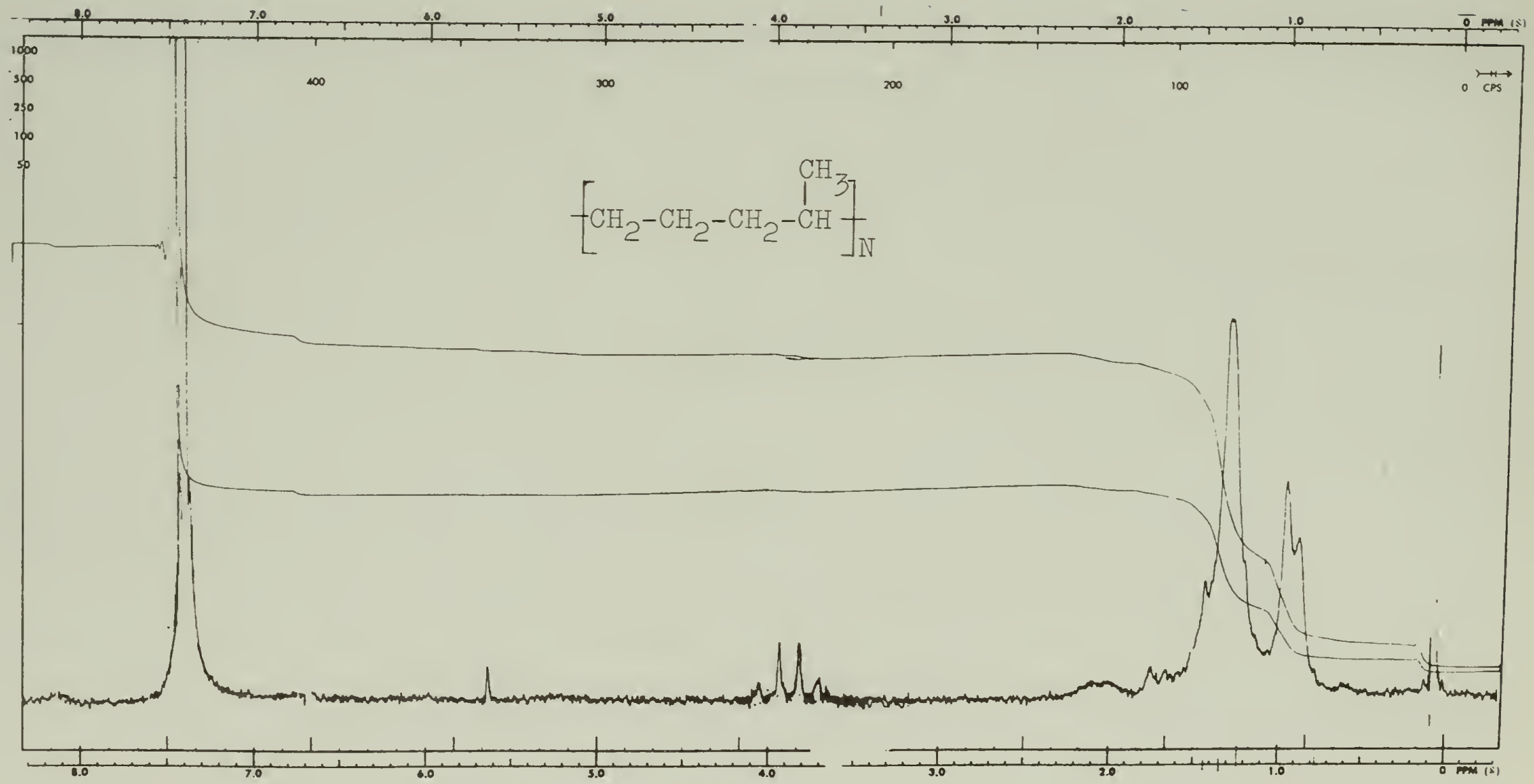
NMR-10. SBS 2 Copolymer (block)



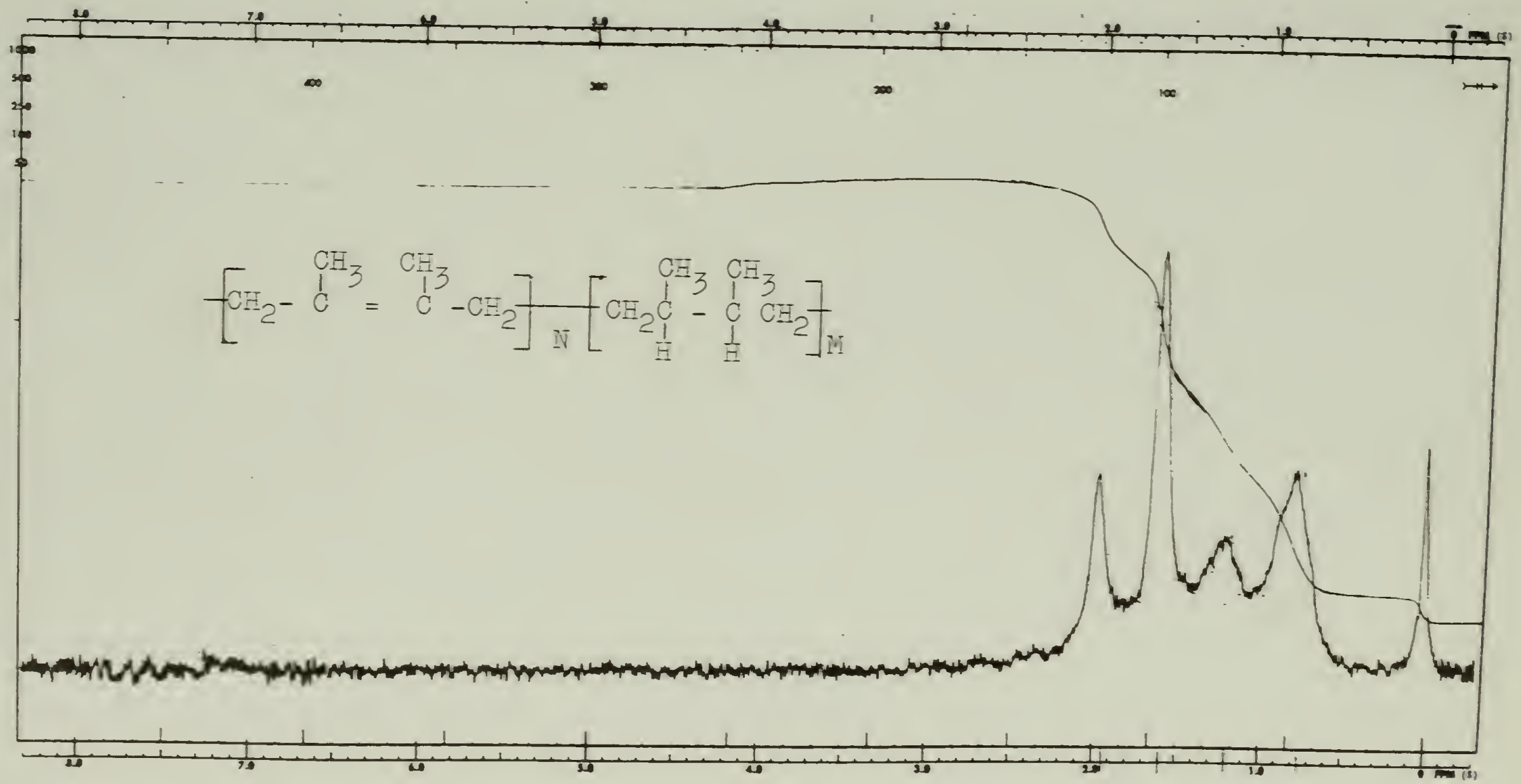
NMR-11. Poly-<u>cis</u> 1,4-isoprene.



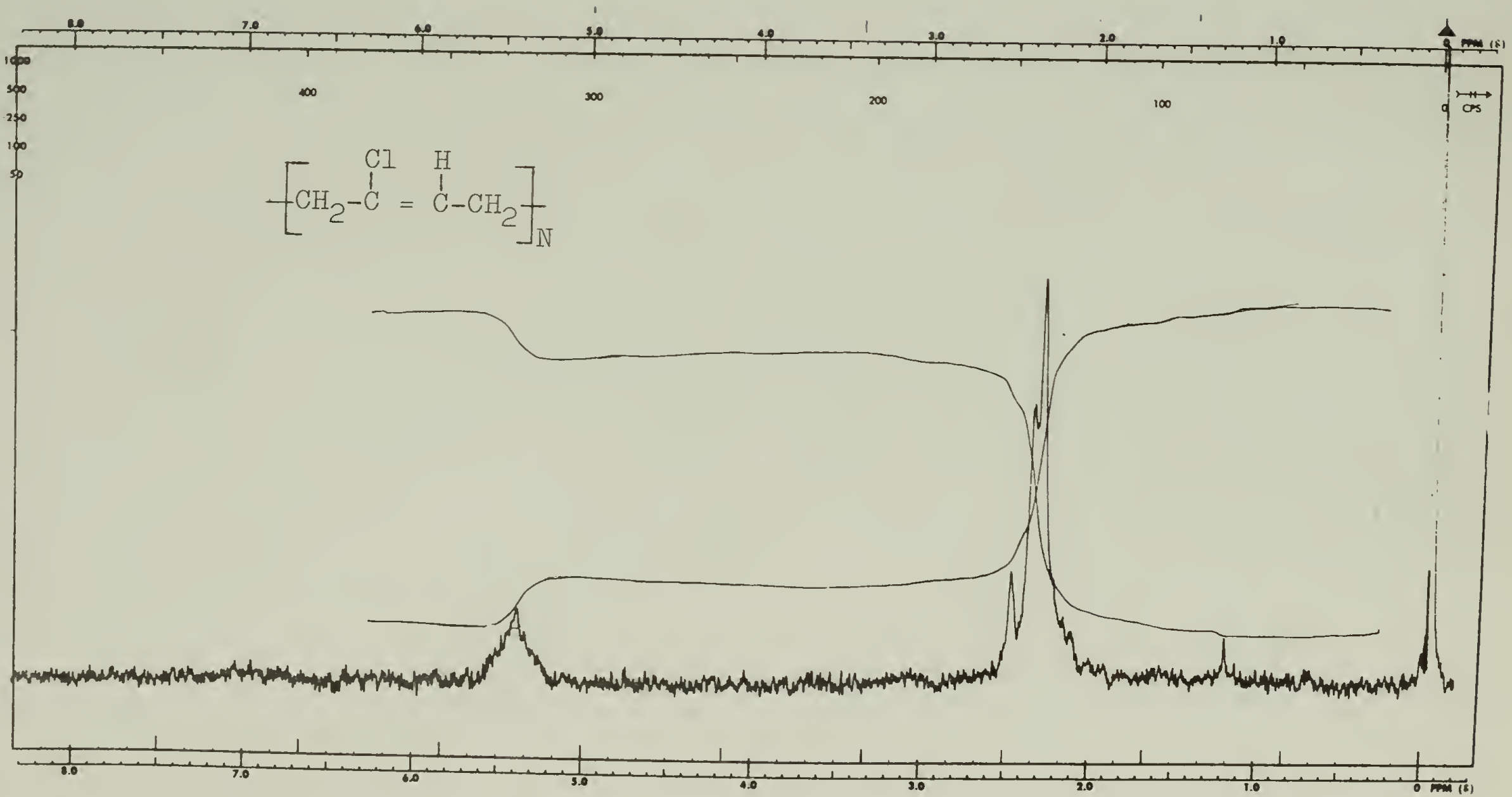
NMR-12. Ethylene-propylene Copolymer



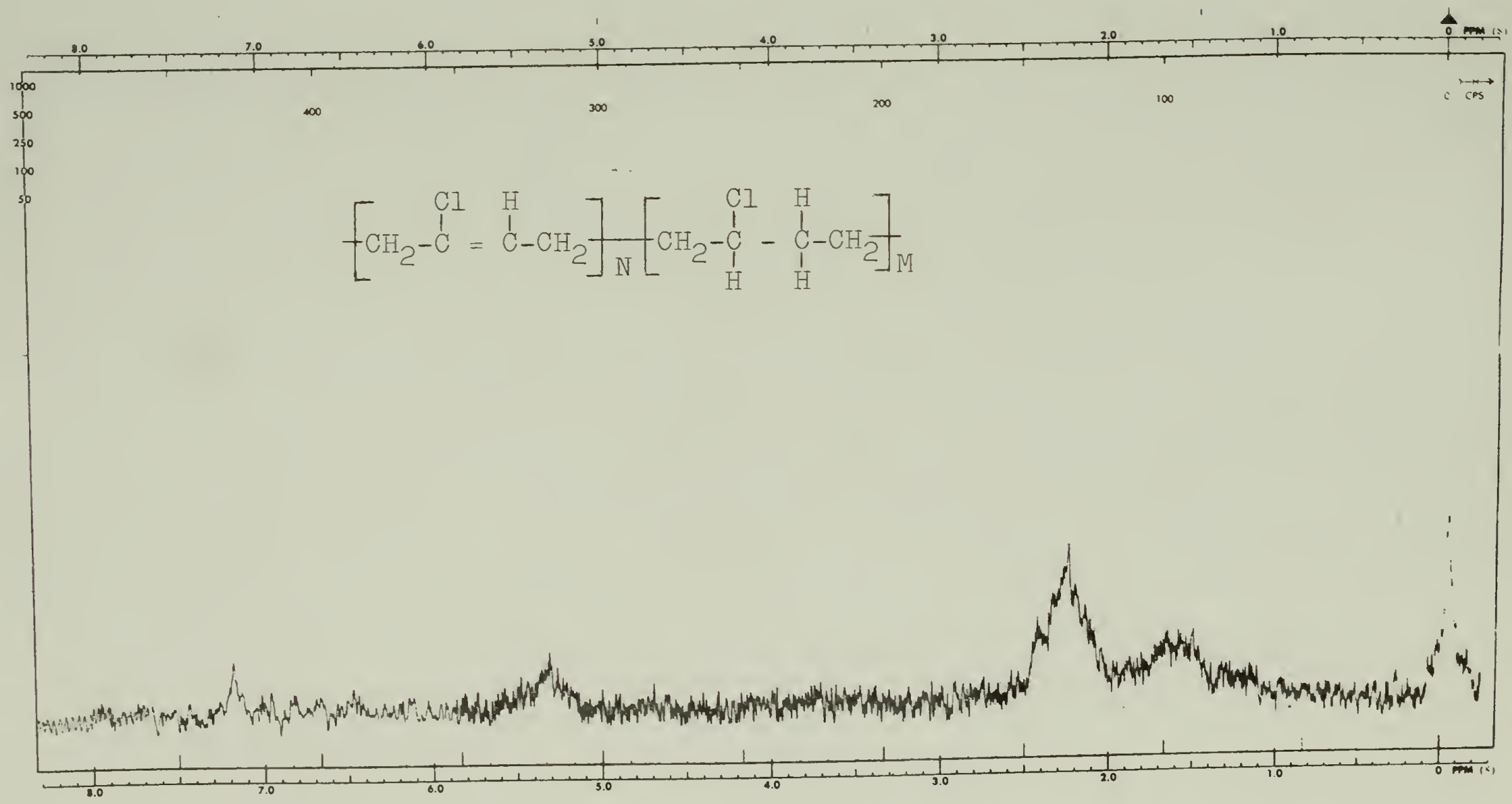
NMR-13. Poly-2,3-dimethylbutadiene (partially hydrogenated)



NMR-14. Polychloroprene

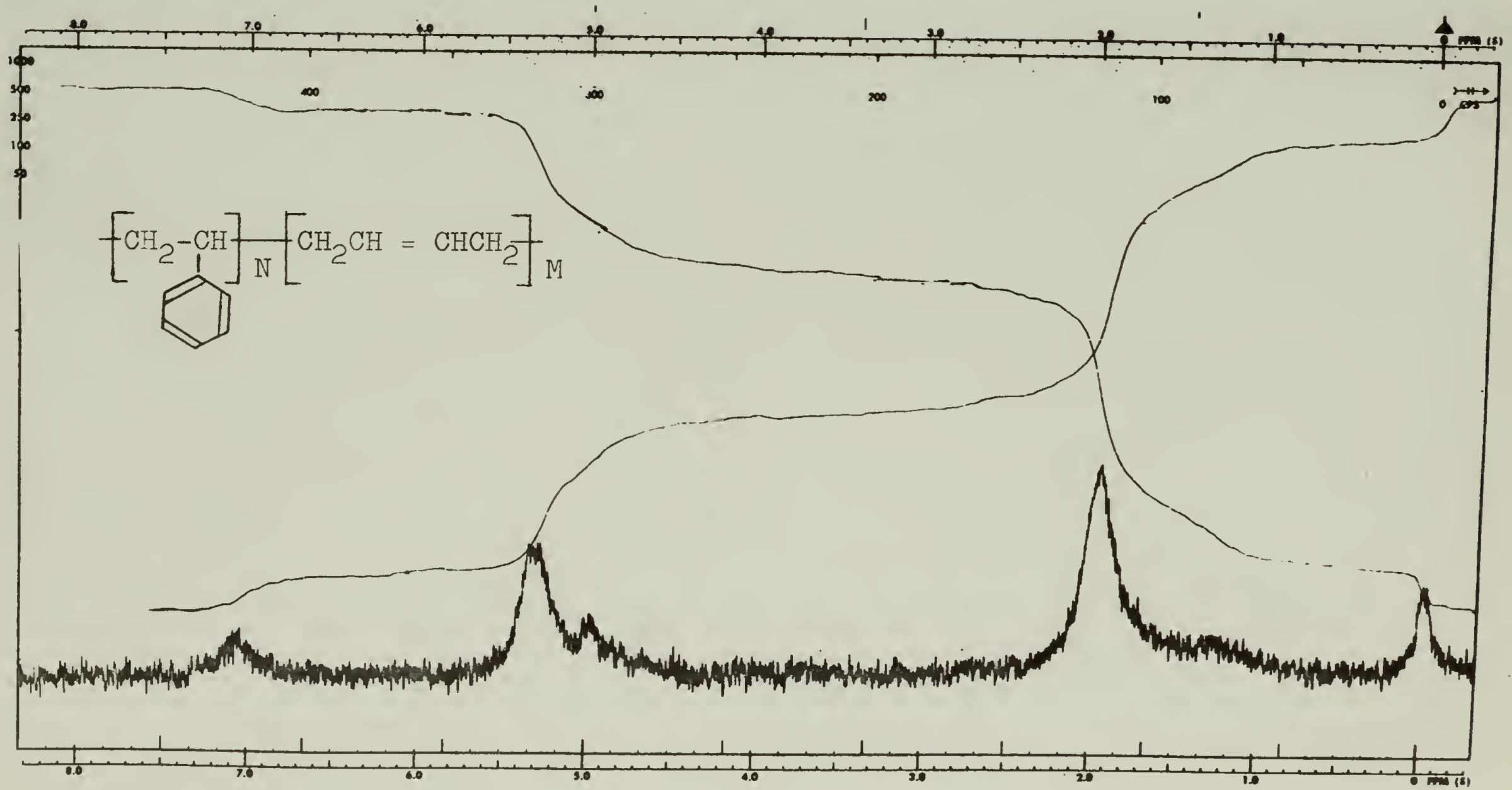


NMR-15. Polychloroprene (partially hydrogenated)

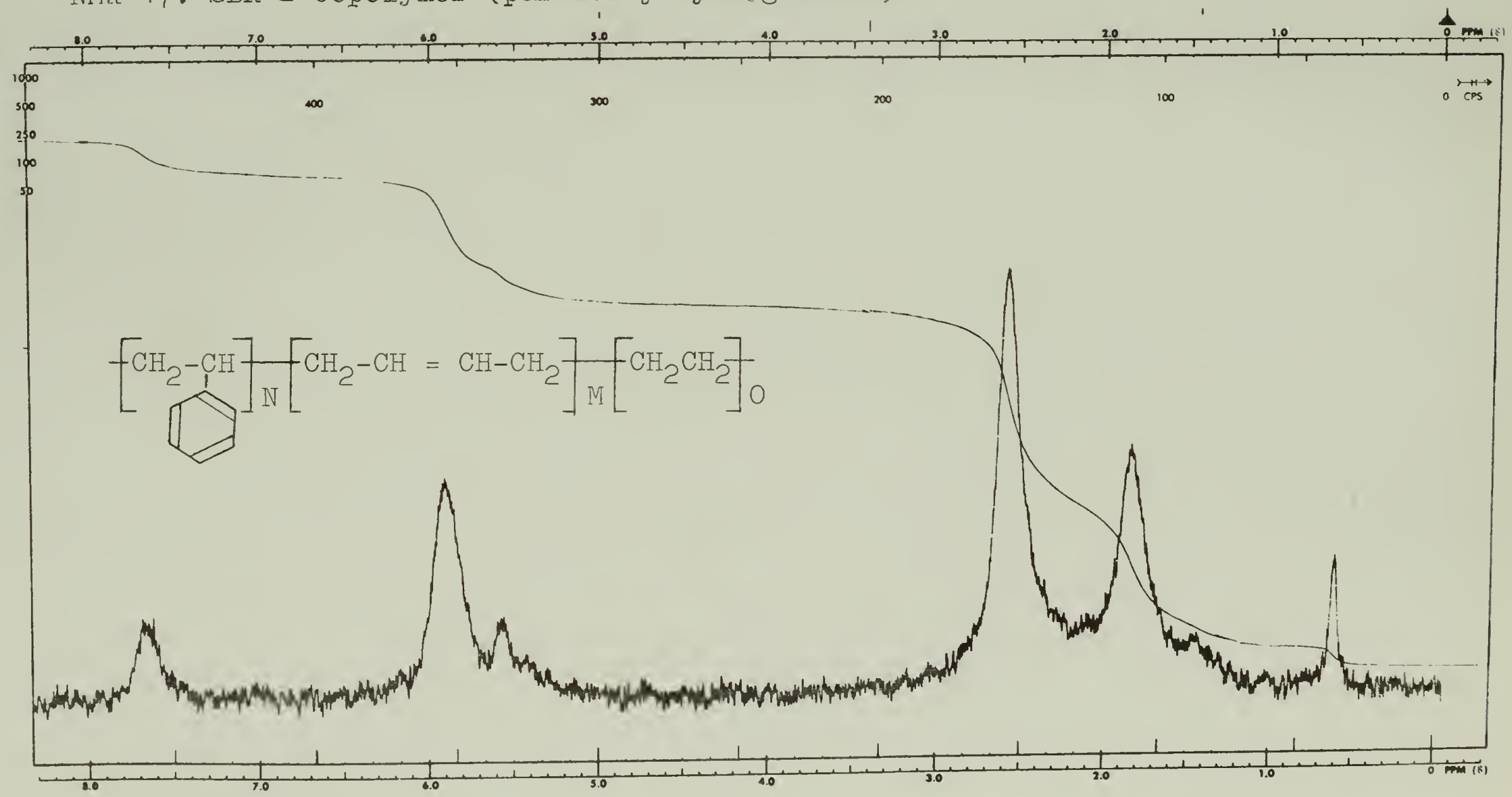


$$\left[CH_2\text{-}\overset{Cl}{\overset{|}{C}} = \overset{H}{\overset{|}{C}}\text{-}CH_2 \right]_N \left[CH_2\text{-}\overset{Cl}{\overset{|}{\underset{H}{\underset{|}{C}}}} - \overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}\text{-}CH_2 \right]_M$$

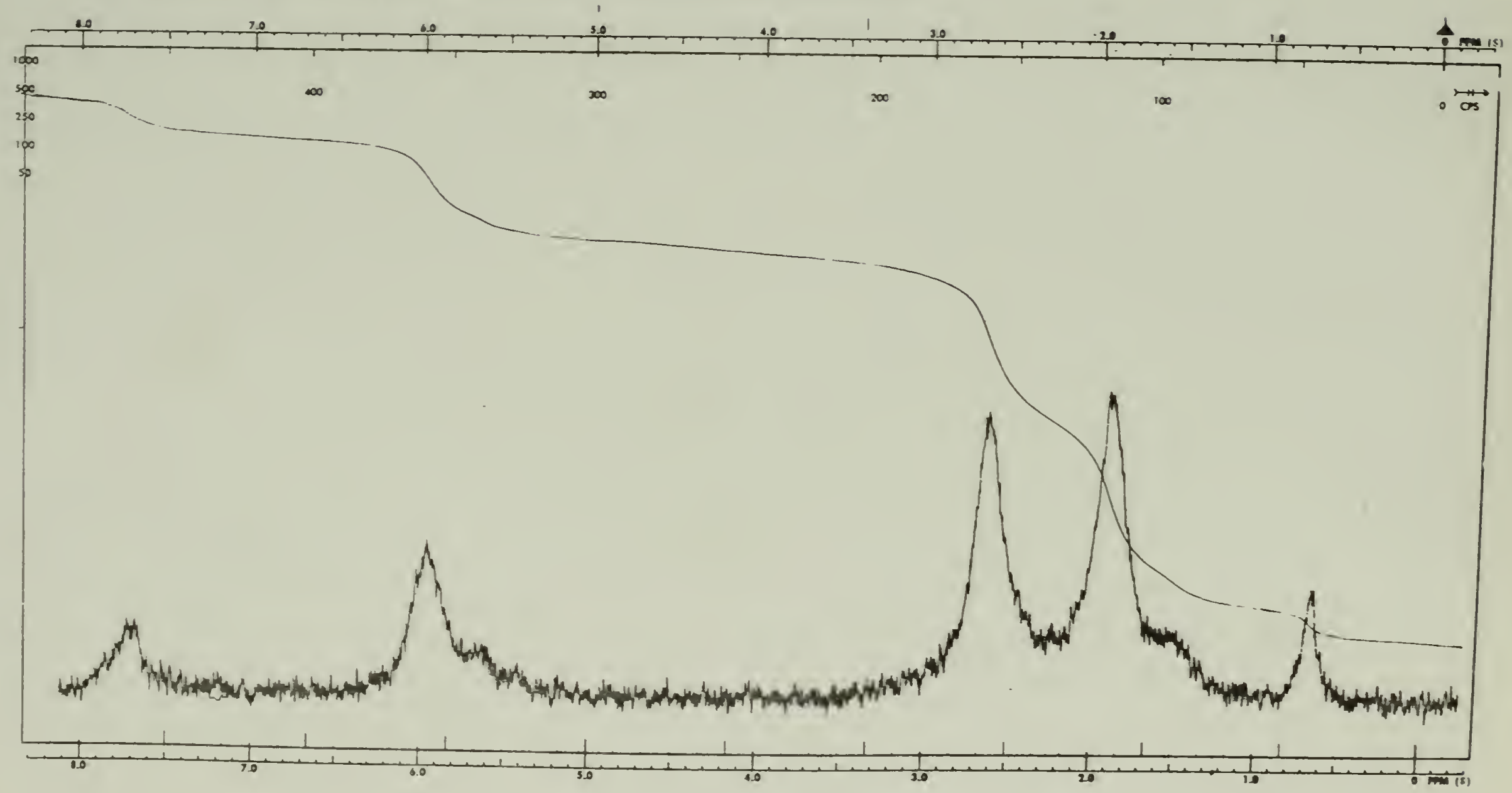
NMR-16. SBR 1 Copolymer



NMR-17. SBR 2 Copolymer (partially hydrogenated)



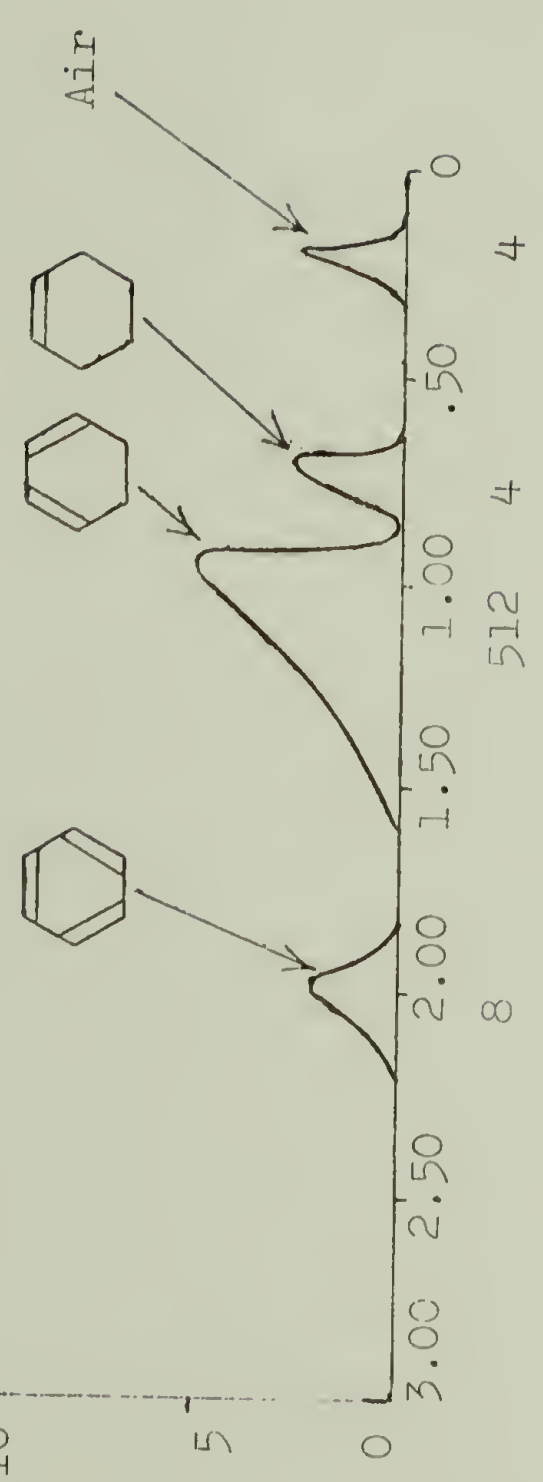
NMR-18. SBR 3 Copolymer (partially hydrogenated)

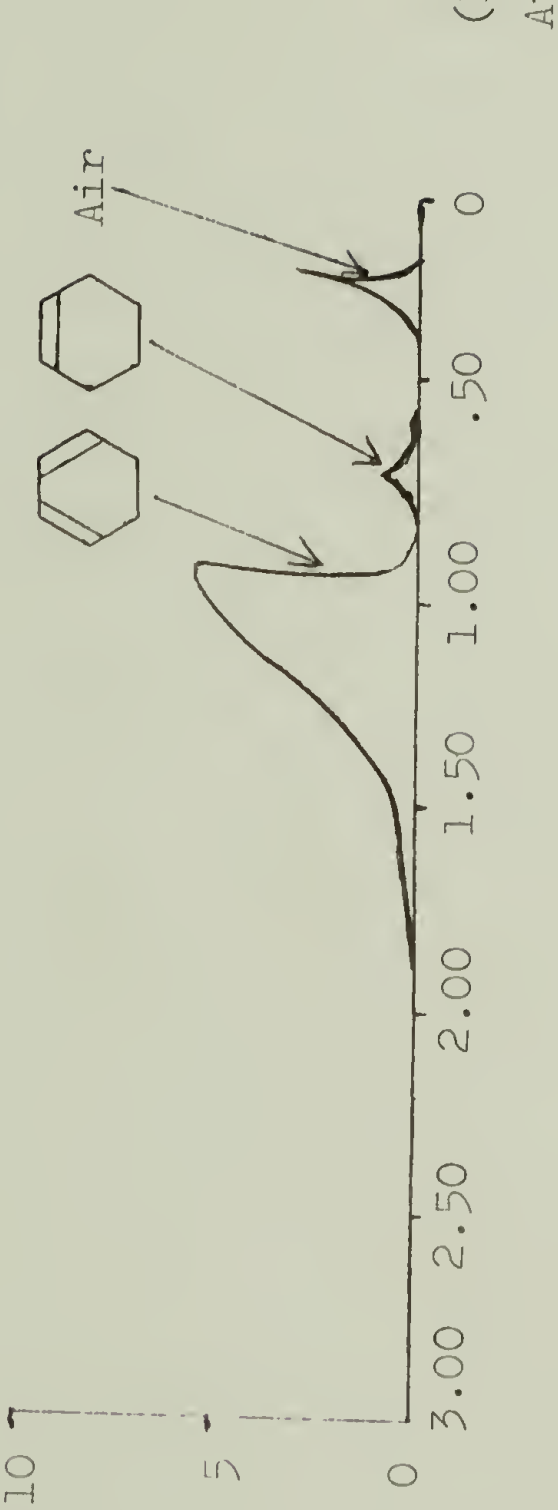


APPENDIX 5

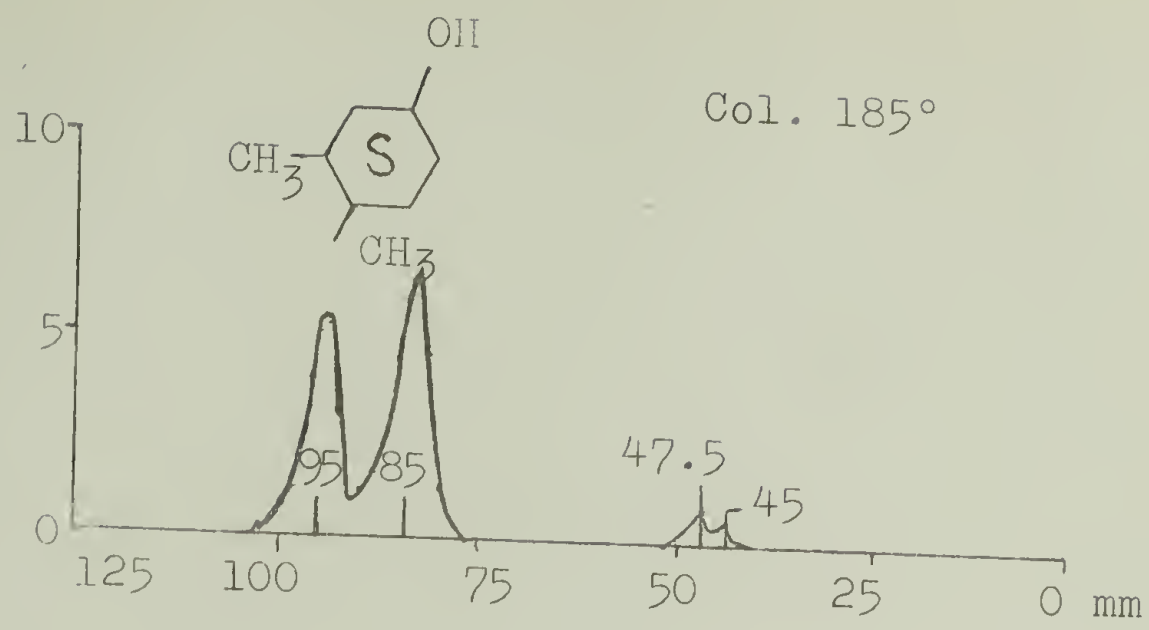
GAS CHROMATOGRAPHY CURVES

GC-1,2. GC Analysis and Purification of 1,3-Cyclohexadiene.

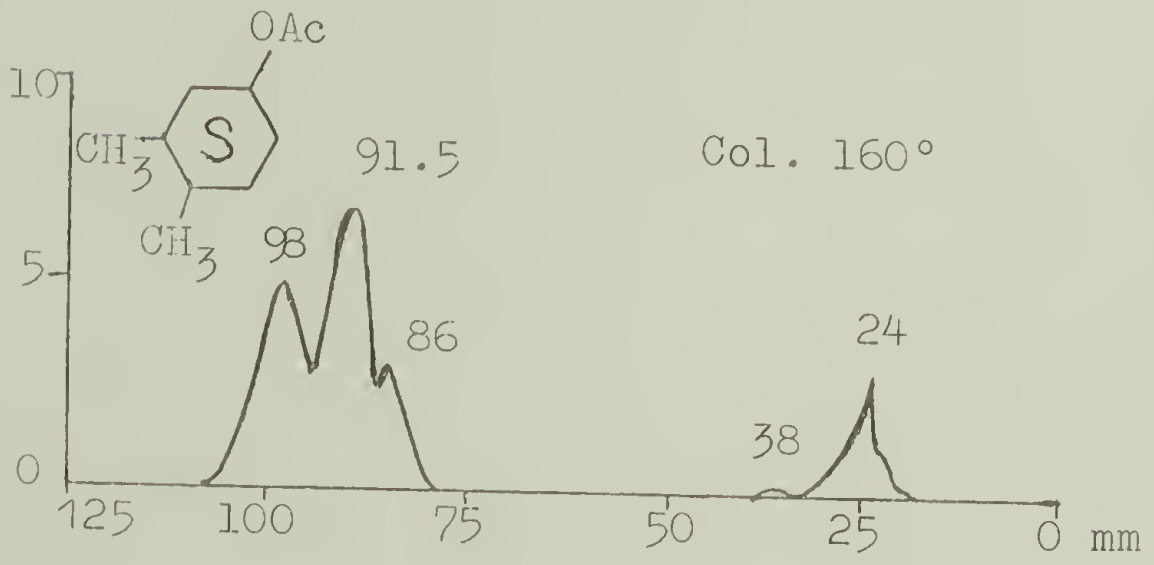




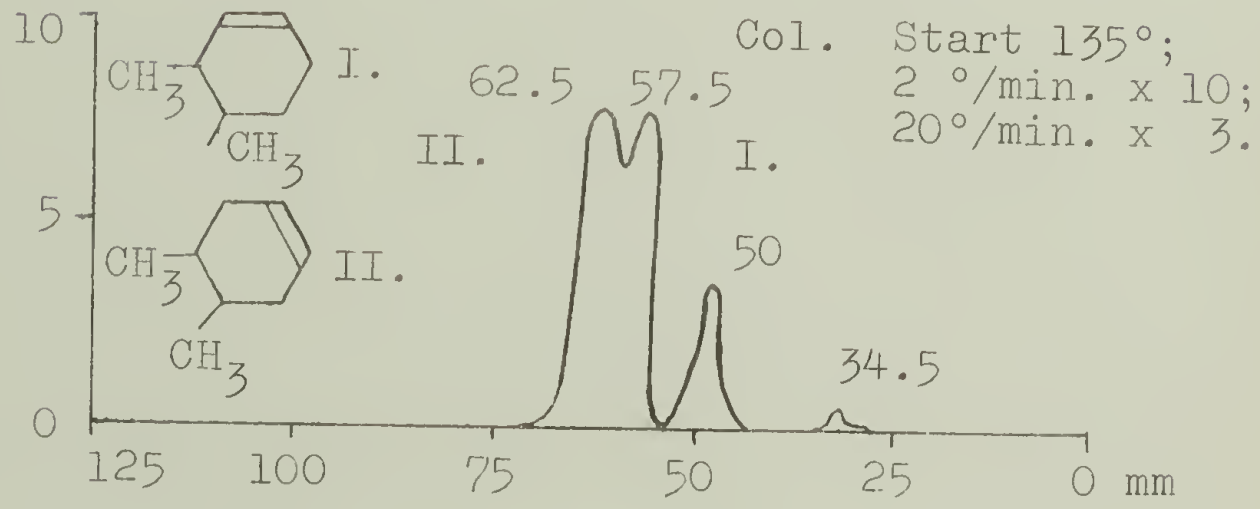
GC-3



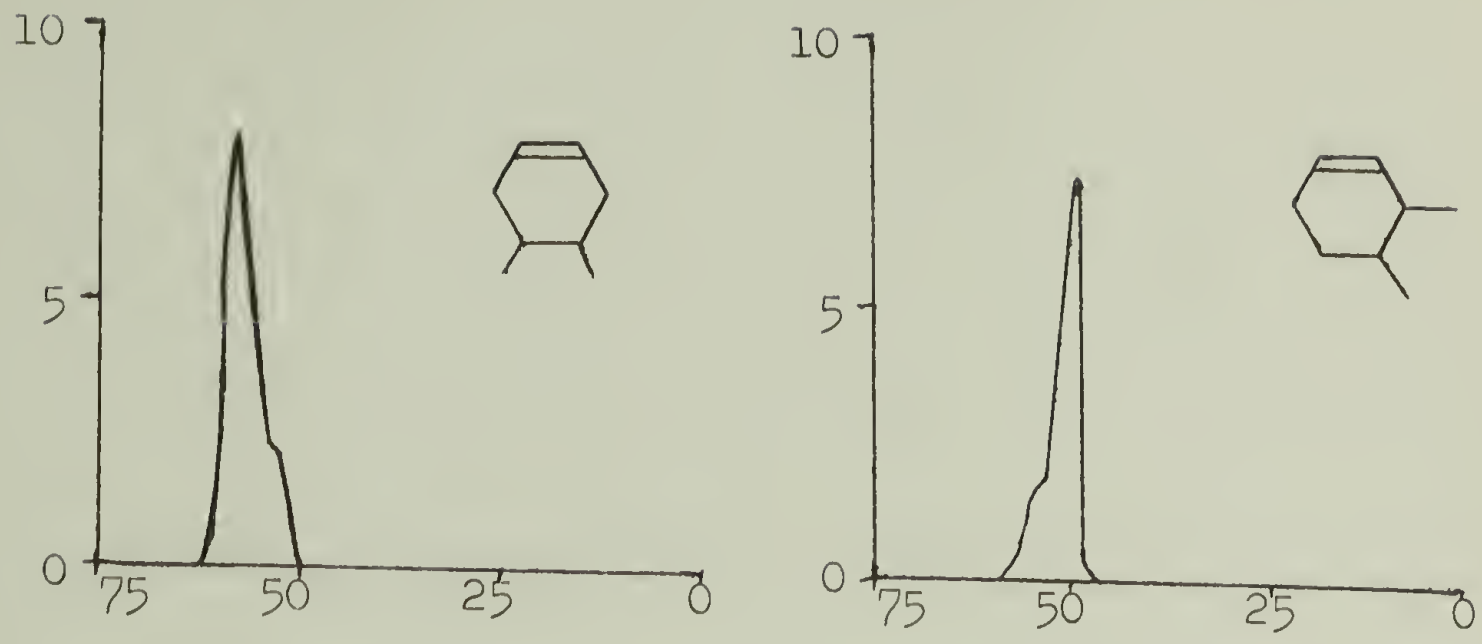
GC-4



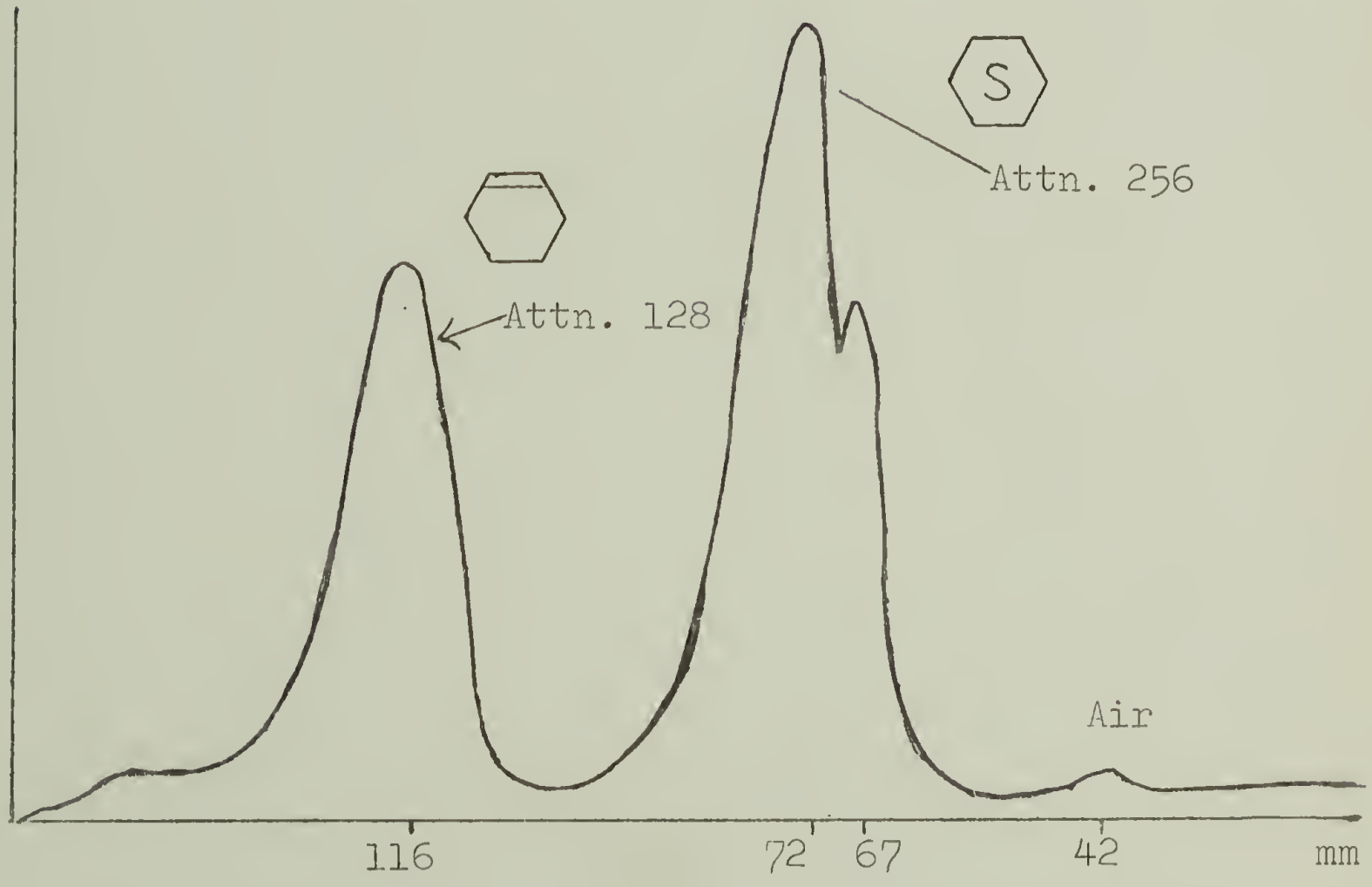
GC-5



GC-3,5. Analysis of 3,4-dimethylcyclohexanol and Derived Materials.



GC-6. Dimethylcyclohexenes of GC-5 after Fractionation.

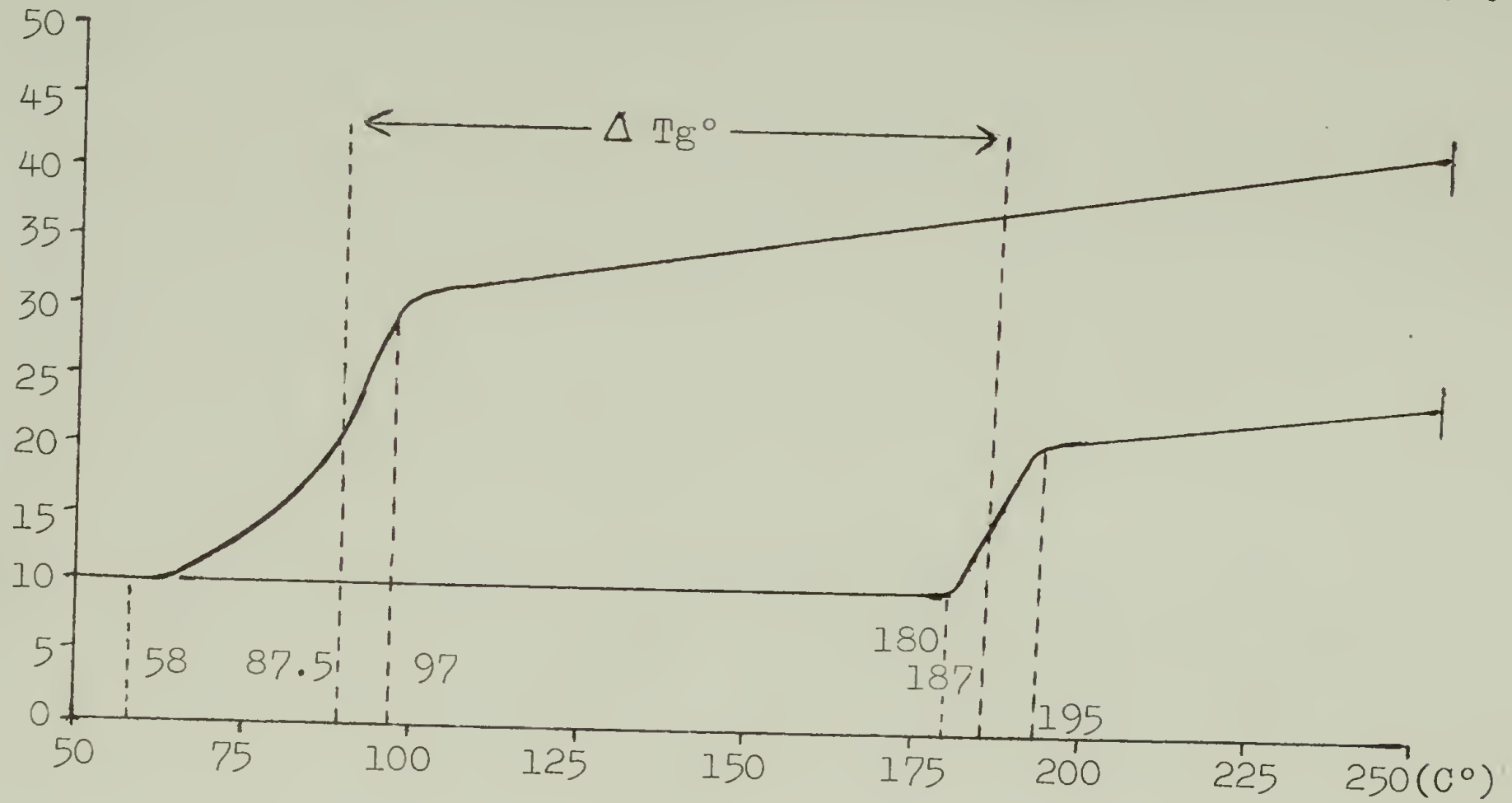


GC-8. Conversion of Cyclohexene to Cyclohexane with p-$CH_3ØSO_2NHNH_2$ in Diglyme.

APPENDIX 6

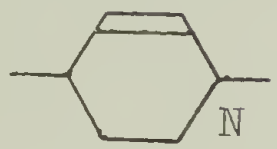
DIFFERENTIAL SCANNING CALORIMETRY CURVES

DSC-1. Effect of Hydrogenation on the Glass Transition Temperature of Polycyclohexene.



Scan Rate: 20°/min. Range: 2

Perkin Elmer: DSC-1b

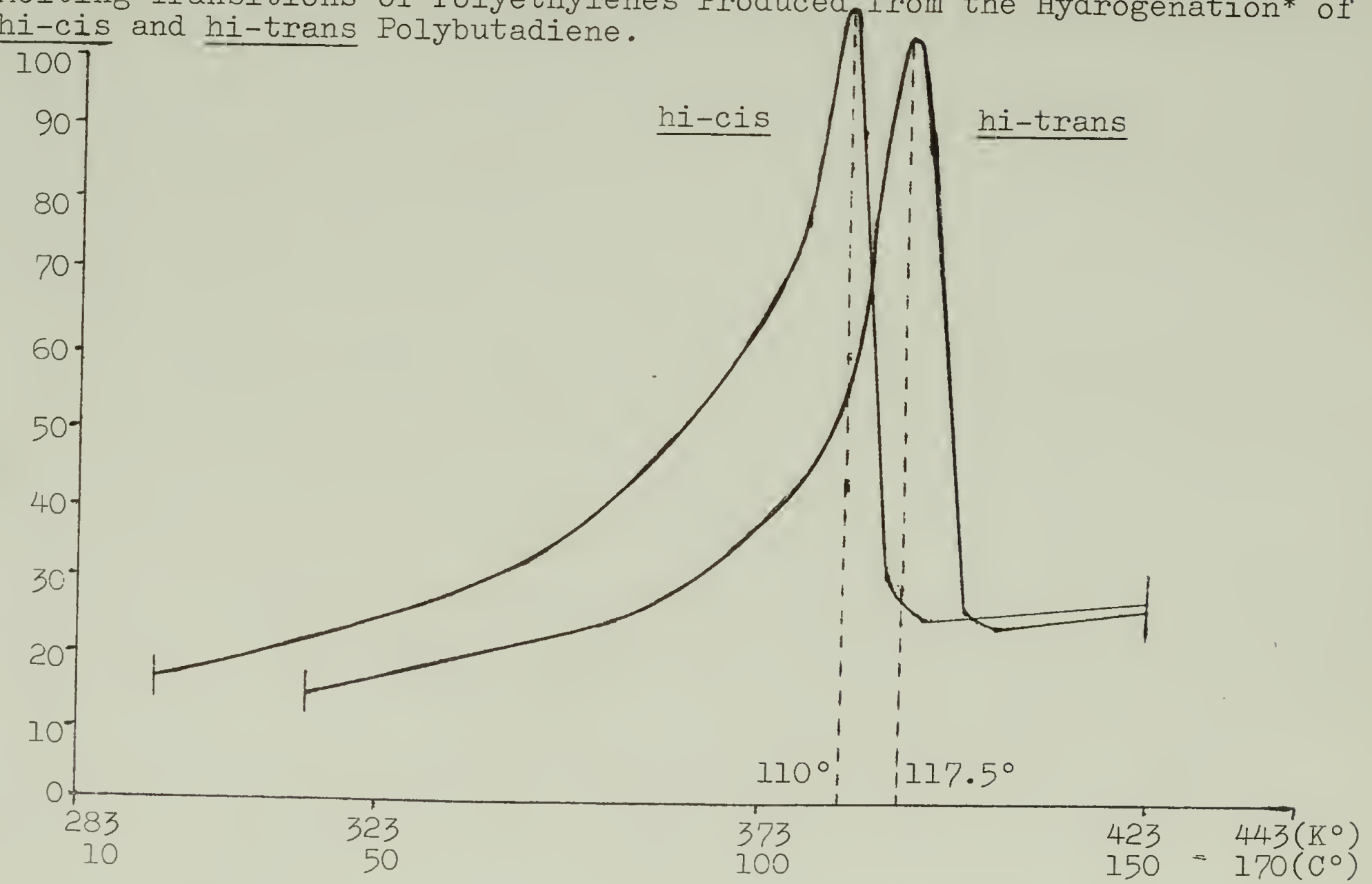
A. 

13.1mg

B. 

12.8mg

DSC-2. Melting Transitions of Polyethylenes Produced from the Hydrogenation* of hi-cis and hi-trans Polybutadiene.



Scan Rate: 20°/min. Range: 8

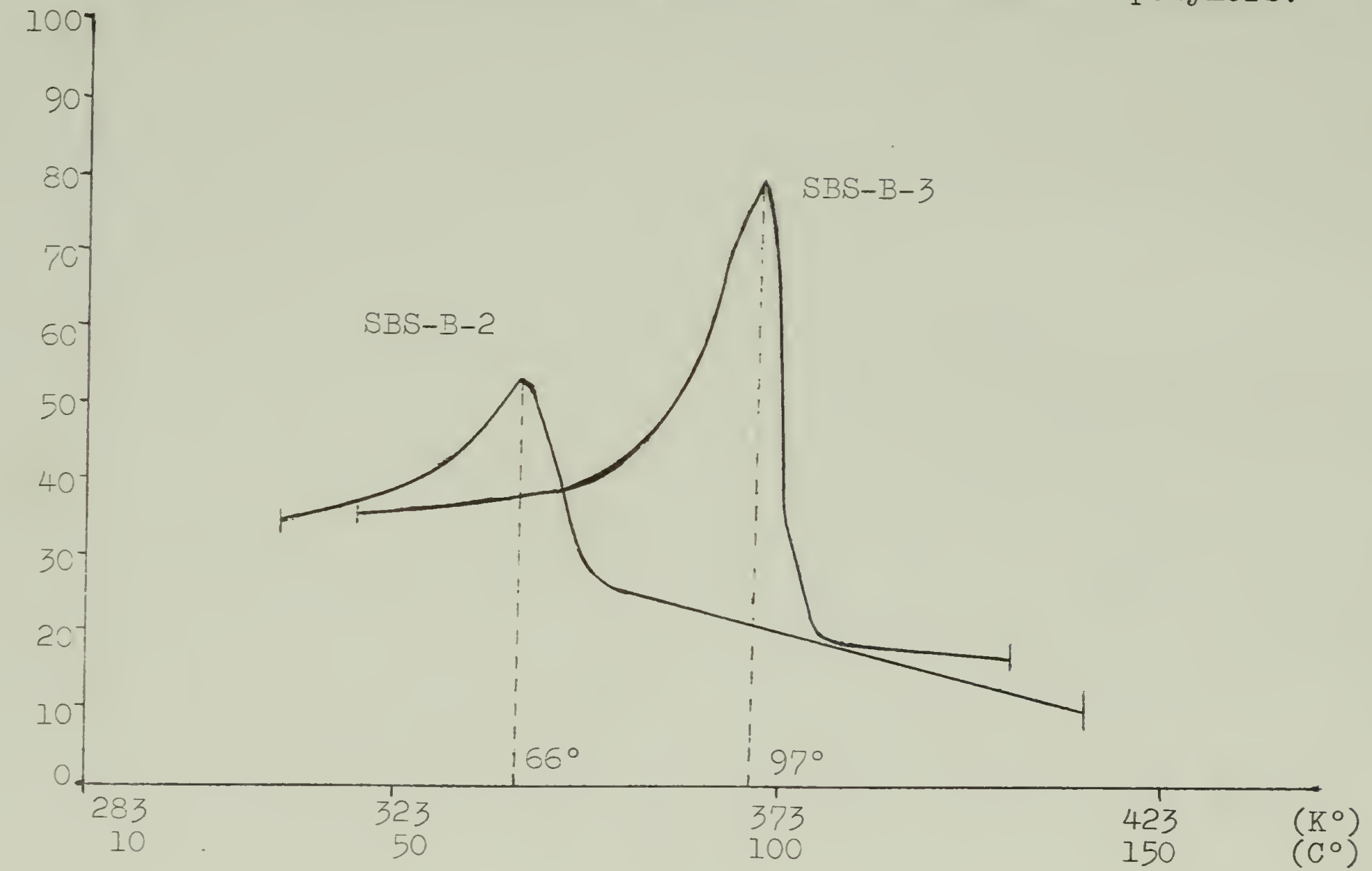
Perkin Elmer: DSC-1b

* Hydrogenation System

4 hours n refluxing xylene

p-TSH = 2/1

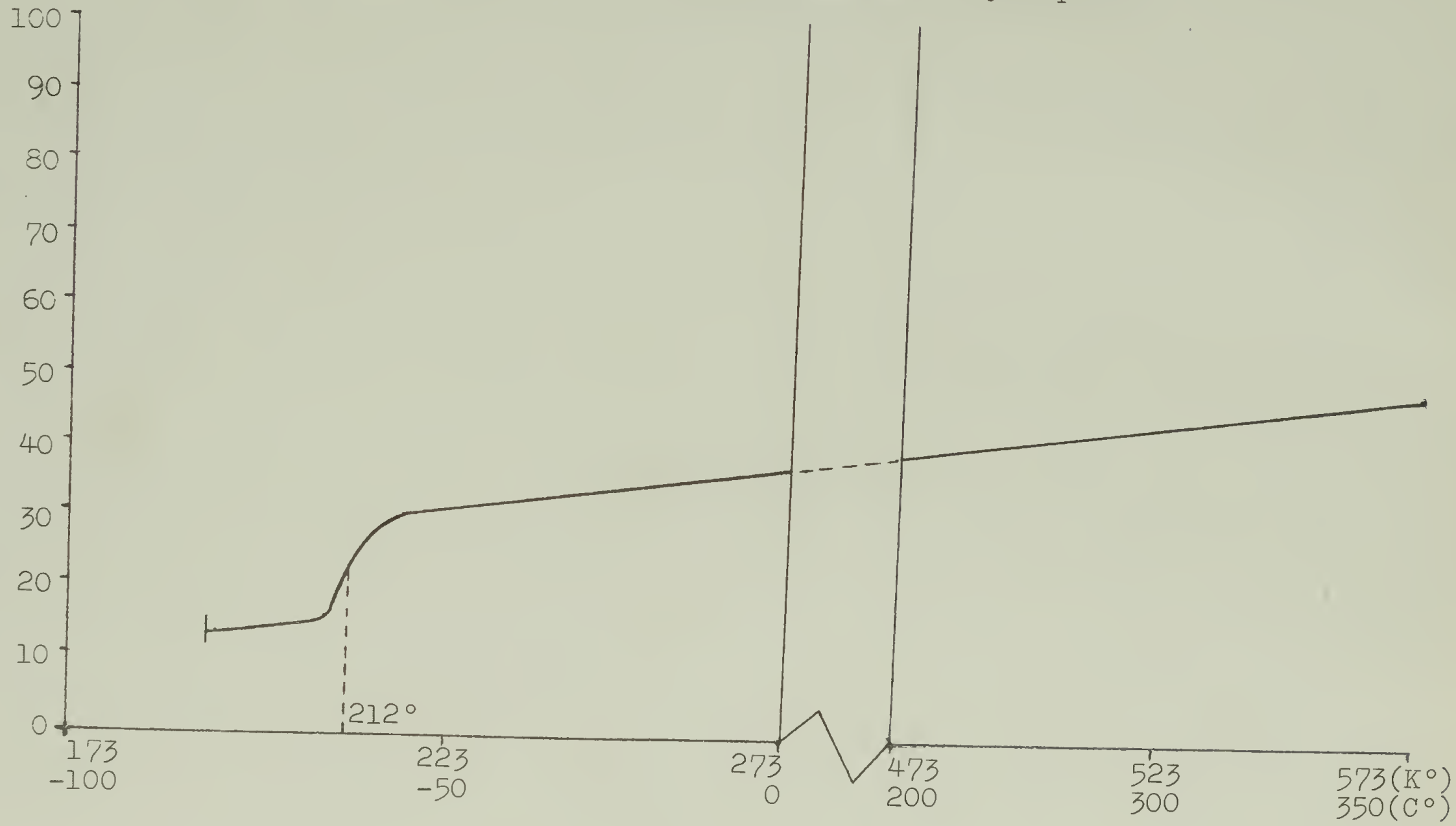
DSC-3. Melting Transitions of Partially Hydrogenated SBS-Block Copolymers.



Scan Rate: 20°/min. Range: 4

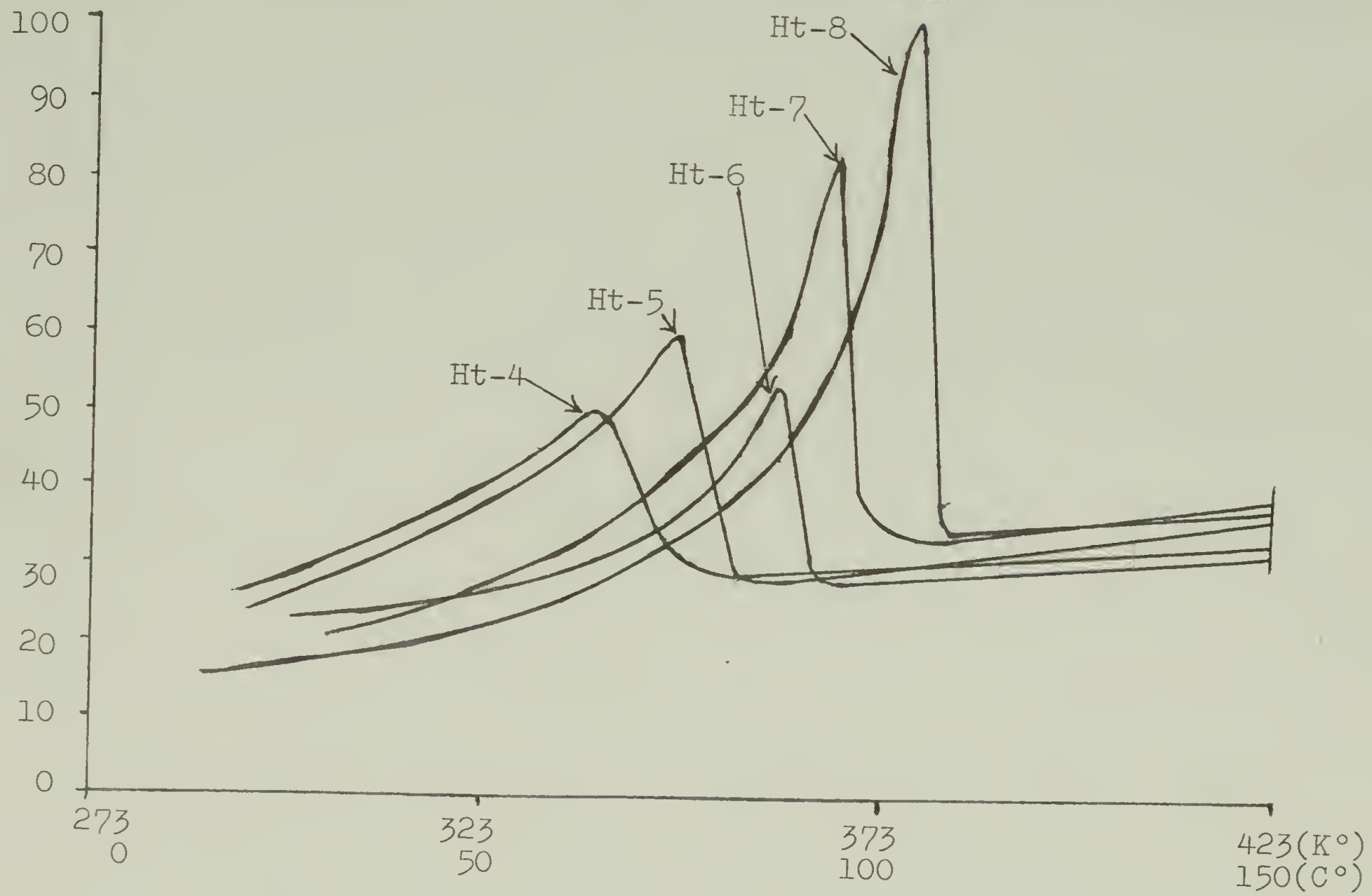
Perkin Elmer: DSC-1b

DSC-4. Glass Transition of Completely Hydrogenated Polyisoprene.



Scan Rate: 20°/min. Range: 4 Coolent: Liquid Nitrogen Perkin Elmer: DSC-1b

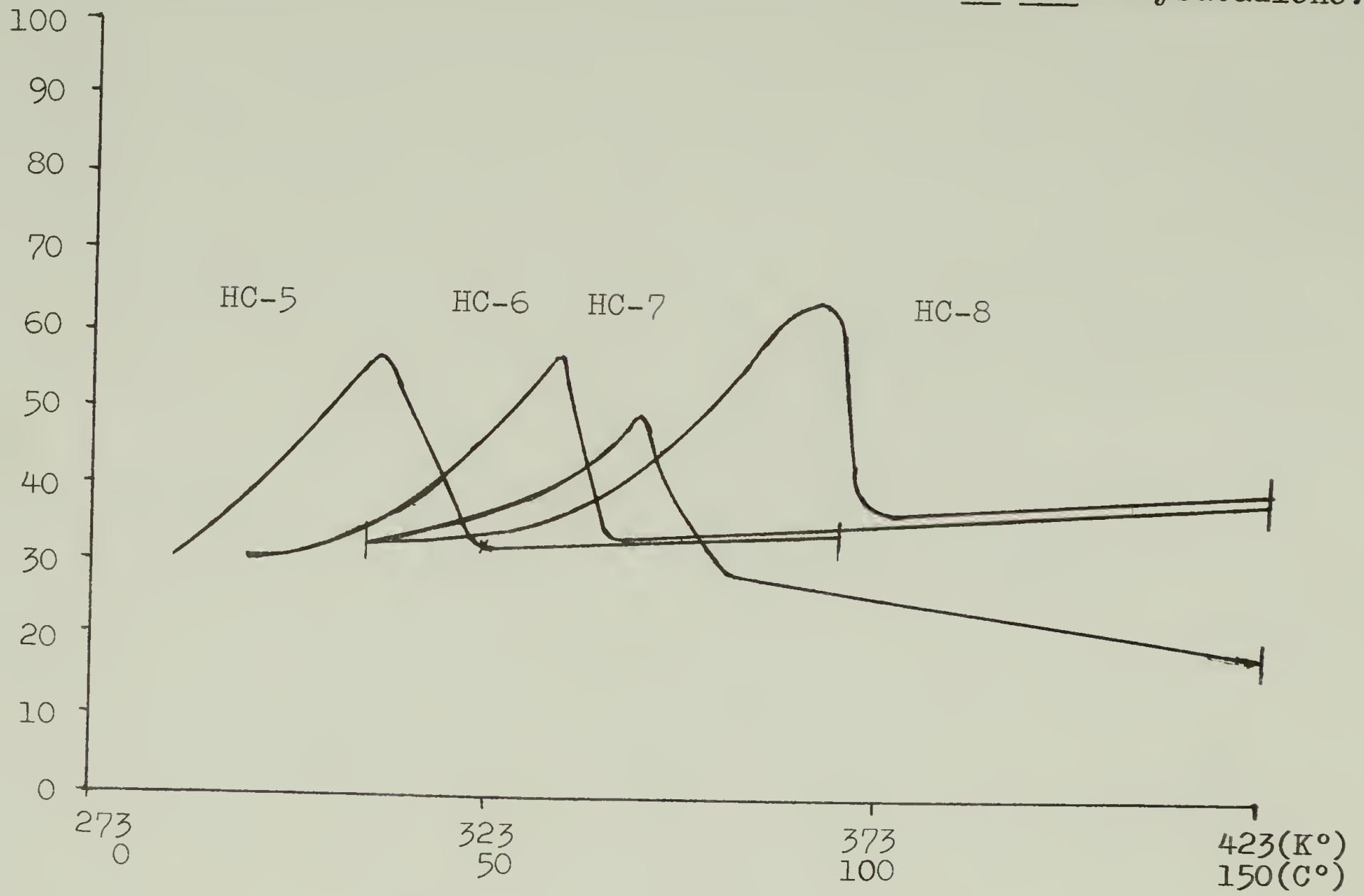
DSC-5. Melting Transitions of Partially Hydrogenated <u>hi-trans</u> Polybutadiene.



Scan Rate: 20°/min. Range: 8 Slope: 540

Perkin Elmer: DSC-1b

DSC-6. Melting Transitions of Partially Hydrogenated <u>hi</u>-<u>cis</u> Polybutadiene.



Scan Rate: 20°/min. Range: 8 Slope: 540 Perkin Elmer: DSC-1B

APPENDIX 7

CATALOG OF POLYMERS AND POLYMERIZATIONS

TABLE A1

POLYCYCLOHEXADIENES SYNTHESIZED BY ANIONIC POLYMERIZATION; SYNTHETIC CONDITIONS

Sample	Tech.[a]	Solvent (mls)	Temp. (°C)	Time (Days)	Additive	(1,3-CHD) (ml)	(nBuLi) (ul;1.6M)
P- 26- 1	VL	THF-50	-78	3.5 hr	none	5-6	50
P- 50- 1	VL	THF-100	room	24 hr	none	5	5000
P- 76- 2	VL	THF-50	-78		TMEDA	1	1500
P-100- 1	C	THF-30	-78	6	none	2.5	300
P-100- 2	C	THF-30	0	7	none	2.5	500
P-100- 3	C	THF-30	30	18 hr	none	2.5	500
P-100- 4	C	$\emptyset CH_3$-30	-78		none	2.5	1000
P-100- 5	C	$\emptyset CH_3$-30	0	7	none	2.5	500
P-100- 6	C	$\emptyset CH_3$-30	30	7	none	2.5	500
P-100- 7	C	nhex-30	-78	7	none	2.5	1000
P-100- 9	C	THF-30	-78	6	BuLi/CO_2	2.5	500
P-100-10	C	THF-30	-78	6	xs BuLi/CO_2	2.5	300
P-100-11	C	$\emptyset CH_3$-30	-78		BuLi/CO_2	2.5	500
P-100-12	C	$\emptyset CH_3$-30	-78	7	TMEDA	2.5	500
P-100-13	C	nhex-30	-78	5	TMEDA	2.5	500
P-102- 1	C	THF-40	-78	3	none	3	700

P-102- 2	C	THF-40	0	3	none	3	700
P-102- 3	C	THF-40	25	6	none	3	700
P-102- 4	C	$\emptyset CH_3$-40	-78	7	none	3	700
P-102- 5	C	$\emptyset CH_3$-40	0	7	none	3	700
P-102- 6	C	C_6H_{12}-40	0	5.5	75 ul TMEDA	3	500
P-102- 7	C	$\emptyset CH_3$-40	25	7	none	3	700
P-102- 8	C	THF-40	-78	3	4 ml BuLi + xs CO_2 (150cc)	3	750
P-102- 9	C	$\emptyset CH_3$-40	0		4 ml BuLi + xs CO_2 (150cc)	3	2200
P-111- 1	VL	$\emptyset CH_3$-75	0	4	none	5	3000 (2.25M)
P-111- 2	VL	Ø-75	0	8	none	5	3000 (2.25M)
P-119- 1	VL	n-hexane-50	-78	3	35 ul TMEDA	10	50 ul (2.25M)
P-119- 2	VL	bulk	room	3	none	residue from	1000 (2.25M)
P-128- 1	VL	98/2 v/v n-hex/THF 100	-78	4	THF	6	175 (2.25M)

[a]VL = Vacuum Line Technique
C = Serum Capped Cylinder Technique

TABLE A2

POLYCYCLOHEXADIENES SYNTHESIZED BY ANIONIC POLYMERIZATION; SAMPLE PROPERTIES

Sample No.	Yield %	Softening Range	C	H
P- 26- 1			89.32	10.14
P- 50- 1		101-106	89.44	10.33
P- 76- 2				
P-100- 1	97.5	124- 28	87.75	9.71
P-100- 2	93	120- 25		
P-100- 3	76	93- 97		
P-100- 4				
P-100- 5	51	98-104		
P-100- 6	15	86- 91	87.75	9.71
P-100- 7	trace			
P-100- 9	97	120- 24	80.90	8.72
P-100-10	66	109-114	88.99	9.35
P-100-11		no yield		
P-100-12	none	none		
P-100-13	8	95-100		

P-102- 1	95	x-link w/heating before melting	90.51	9.48
P-102- 2	92.5	120- 26	89.61	9.88
P-102- 3	60	104-110	90.02	9.88
P-102- 4	no MeOH insol.			
P-102- 5	40	104-112	89.32	9.63
P-102- 6	56	x-link w/heating before melting	89.23	9.46
P-102- 7	89		89.83	9.06
P-102- 8	96	132- 38	89.38	9.84
P-102- 9	no MeOH insol.			
P-111- 1	11	91- 96	89.80	10.10
P-111- 2	100	99-103	90.07	10.29
P-119- 1	small	132-140		
P-119- 2		105-110	89.62	10.11 0 = 0.39
P-128- 1	20	135-140	89.70 0 = 0.13	10.10 ash = nil

TABLE B

POLYCYCLOHEXENES FORMED BY THE HYDROGENATION
OF POLYCYCLOHEXADIENES

Sample No.	Elemental Analysis				F. J. Sft. Pt.	% Conversion by		
	C	H	O	Other		IR	NMR	Elemental Analysis[a]
P- 32-2	87.59	10.25	. .	2.16	. .	5	. .	15
P- 39-1	84.61	10.41	. .	4.98	. .	48	. .	40
P- 62-1	. .	. .	. .	. .	. .	78	. .	. .
P- 70-1	85.52	11.73	. .	2.75	197-205	97	. .	89
P- 79-1	87.27	11.12	. .	1.60	230-240	100	. .	(57)
P- 52-1	85.56	11.99	. .	2.45	214-220	95	. .	98
P- 54-1	87.15	11.98	0.48	0.39	192-195	95	100	91
		S,ash = nil						
P-125-1	85.52	10.98	1.87	. .	240-245	. .	100	85
		ash = 1.71						
P-115-1	87.69	11.97	. .	0.34	230-235	. .	100	85
P-114-1	87.31	11.87	. .	0.86	187-192	. .	100	100
P-124-1	86.67	12.46	. .	0.87	193-198	. .	. .	. .
P-129-2	81.24	10.02	6.89	1.89	100-105	. .	. .	. .
Theoretical	87.95	12.05	. .	. .	?	100	100	?

[a]See Tables C and D for procedure and calculations.

TABLE C

CALCULATION OF PER CENT HYDROGENATION OF POLYCYCLOHEXADIENES BY INFRARED SPECTROSCOPY

Procedure: The infrared spectra of polycyclohexenes and their precursor polycyclohexadienes were determined on sample solutions of known concentrations. The adsorbance at 3015 cm^{-1} (olefinic C=C-H stretch) was calculated from the transmittance and normalized to account for concentration differences. Per cent conversion, C%, then equals $100(1-\frac{A_{prod}}{A_{precursor}})$

Sample[a]	IR No.	T_{3015} (%)	A_{3015}	Conc. (mg/10ml CS_2)	Normalized A_{3015}	$\%R_{xn.}$
P-26-1	22a	62.0	0.208	273.0	0.076	
P-32-2	24	85.5	0.068	86.0	0.079	5
P-26-1	22a	44.0	0.356	418.5	0.085	
P-39-1	25a	67.0	0.174	392.0	0.044	48
P-50-1	22a	45.0	0.347	313.0	0.110	
P-62-1	25b	80.0	0.097	409.0	0.024	78
P-50-1	22a	45.0	0.347	313.0	0.110	
P-70-1	25c	98.0	0.01	409.0	0.003	97
P-78-1	22b	71.0	0.148	310.0	0.048	
P-79-1	25d	100.0	0.0	406.7	0.0	100
P-52-1	25e	97.0	0.014	340.0	0.004	95-100
P-50-2	22a	45.0	0.347	313.0	0.110	
P-54-1	27	97.0	0.014	307.0	0.005	95

[a]First member of each pair refers to the starting material.

TABLE D

CALCULATION OF PER CENT HYDROGENATION OF POLYCYCLOHEXADIENES BASED UPON ELEMENTAL ANALYSIS

Procedure: The percentage of unsaturation (residual olefin content) may be calculated from the relation

$$U\% = \frac{(1.688f_c - f_h)}{0.142} \times 100$$

where f_c and f_h are respectively the observed mole fractions of carbon and hydrogen in the product polymer. This is derived as follows: Theoretically, for polycyclohexene,

% C = 87.7 % H = 12.3

and for polycyclohexadiene,

% C = 89.9 % H = 10.1.

The mole fractions of C and H theoretically present in each pure homopolymer are:

Polycyclohexadiene,

Moles C = 89.9/12 = 7.43; mole fraction C = 0.425

Moles H = 10.1/ 1 = 10.10; mole fraction H = 0.575

Polycyclohexene,

Moles C = 87.7/12 = 7.30; mole fraction C = 0.372

Moles H = 12.3/ 1 = 12.3; mole fraction H = 0.628.

Partially reduced polycyclohexadienes may be considered to be made up of contributions from reduced and non-reduced segments so the following relations hold:

$$f_c = 0.372\ (\%S) + 0.425\ (\%U)$$

$$f_h = 0.628\ (\%S) + 0.575\ (\%U)$$

% S = % saturated % U = % unsaturated

Simultaneous solution and rearrangement gives

$$0.142\ U = 1.688f_c - f_h$$

$$\%U = \frac{(1.688f_c - f_h)}{0.142} \times 100$$

Therefore,

$$\%\ R'xn. = (100-U)\ \%$$

Results

Sample	%C	%H	Moles C
P- 32-2	87.59	10.25	7.30
P- 39-1	84.61	10.41	7.05
P- 70-1	85.52	11.73	7.13
P- 79-1	87.27	11.12	7.27
P- 52-1	85.56	11.99	7.13
P- 54-1	87.15	11.98	7.27
P-115-1	87.69	11.97	7.32
P-114-1	87.31	11.87	7.27
P-124-1	86.67	12.46	7.23

Moles H	f_c	f_h	%U	%R
10.25	0.417	0.583	85	15
10.41	0.404	0.596	60	40
11.73	0.378	0.622	11	89
11.12	0.395	0.605	43	57
11.99	0.373	0.627	2	98
11.98	0.377	0.623	9	91
11.97	0.380	0.620	15	85
11.87	0.380	0.620	15	85
12.46	0.368	0.632	0	100

TABLE E

CALCULATION OF PER CENT REDUCTION OF PARTIALLY HYDROGENATED CIS AND TRANS POLYBUTADIENES BASED UPON ELEMENTAL ANALYSIS

Procedure: The percentage of unsaturation may be calculated from the relation

$$U\ \% = \frac{(2f_c - f_h)}{0.2} \times 100$$

where f_c and f_h are respectively the observed mole fractions of carbon and hydrogen in the product polymer. The derivation is analgous to that given for polycyclohexene in Table D.

For polybutadiene,

% C = 88.9 % H = 11.1

and for polyethylene,

% C = 85.7 % H = 14.3.

Therefore, for polybutadiene

Moles C = 88.9/12 = 7.41; mole fraction C = 0.40

Moles H = 11.1/ 1 = 11.10; mole fraction H = 0.60

and for polyethylene,

Moles C = 85.7/12 = 7.15; mole fraction C = 0.333

Moles H = 14.3/ 1 = 14.30; mole fraction H = 0.667.

$$f_c = 0.333\ (\%S) + 0.400\ (\%U)$$

$$f_h = 0.667\ (\%S) + 0.600\ (\%U)$$

% S = % Saturated % U = % Unsaturated

Simultaneous solution and rearrangement gives

$$\%\ U = \frac{(2f_c - f_h)}{0.2} \times 100$$

TABLE E1, CIS-1,4-POLYBUTADIENE

Sample	%C	%H	Moles C
HC-1	88.02	10.74	7.33
HC-2	85.48	11.21	7.12
HC-3	85.62	11.80	7.18
HC-4	84.14	12.06	7.02
HC-5	83.95	12.23	6.99
HC-6	83.91	13.00	6.98
HC-7	83.04	12.94	6.92
HC-8	81.42	12.81	6.77

TABLE E2, TRANS-1,4-POLYBUTADIENE

Sample	%C	%H	Moles C
Ht-1	88.03	10.96	7.34
Ht-2	85.94	11.59	7.16
Ht-3	84.65	12.17	7.06
Ht-4	84.13	12.65	7.01
Ht-5	83.80	12.77	6.97
Ht-6	85.29	12.71	7.11
Ht-7	82.38	12.90	6.86
Ht-8	82.52	13.05	6.88

Moles H	f_c	f_h	% U	% R'xn
10.74	0.406	0.594	109.0	0.0
11.21	0.388	0.612	82.0	18.0
11.80	0.378	0.622	67.0	33.0
12.06	0.368	0.632	52.0	48.0
12.23	0.363	0.637	44.5	55.5
13.00	0.349	0.651	23.5	76.5
12.94	0.348	0.652	22.0	78.0
12.81	0.346	0.654	19.0	81.0

Moles H	f_c	f_h	% U	% R'xn
10.96	0.401	0.599	101.5	0.0
11.59	0.382	0.618	73.0	27.0
12.17	0.367	0.633	50.5	49.5
12.65	0.357	0.643	35.5	64.5
12.77	0.353	0.647	29.5	70.5
12.71	0.359	0.641	35.7	64.3
12.90	0.347	0.653	20.5	79.5
13.05	0.345	0.655	17.0	83.0

TABLE F1

PER CENT REDUCTION OF SBR COPOLYMER BASED UPON ELEMENTAL ANALYSIS

Sample	% C (Observed)	% H (Observed)	% C (Corr. to 100% C+H)	% H (Corr. to 100% C+H)	H inc. per 100g C+H	%R'xn[b]
SBR-1						
Calculated[a]	. .	. .	89.51	10.49	. .	. .
Observed[c]	88.41	10.40	89.48	10.52	. .	. .
SBR-2	88.61	10.95	88.63	10.9	0.42	16
SBR-3	88.06	10.87	88.96	10.97	0.45	17
SBR-4	87.62	11.38	88.50	11.49	0.97	37
SBR-5	86.49	11.56	88.22	11.80	1.28	48
SBR-6	86.36	12.32	87.48	12.48	1.96	74
SBR-7	85.61	12.20	87.50	12.50	1.98	75
SBR-8	84.56	12.64	87.00	13.00	2.48	94
Calculated for 100% Conversion[a]	. .	. .	86.85	13.15	2.65	100

[a] Assumes composition 82% by weight butadiene and 18% by weight styrene quoted by supplier.

[b] Calculated from % R'xn. = $\frac{(\text{H inc})\text{OBS}}{(\text{H inc})\text{CALC.}}$ X 100%

[c] O = 0.94% ash = 0.27% (after reprecipitation).

TABLE F2

PER CENT REDUCTION OF PARTIALLY HYDROGENATED SBR COPOLYMERS BASED UPON NMR ANALYSIS

Procedure: The ratio, (R), of aliphatic, (A), to vinyl, (V), protons present in a SBR sample was determinable by NMR analysis was used to calculate the per cent hydrogenation as follows: the 90/10 mole ratio of polybutadiene to styrene present in the copolymer requires 9 butadiene segments for each styrene unit. At all stages of hydrogenation each styrene unit possesses three aliphatic protons, while the four aliphatic protons in a butadiene segment increases to eight upon hydrogenation. Therefore, the average number of aliphatic protons present for each butadiene unit is 4 + 4x where x is the fraction hydrogenated. Similarly, the vinyl contribution per each butadiene unit is reduced from 2 to 0 during reduction so on the average each butadiene segment contributes 2-2x vinyl resonances. At the 90/10 mole ratio present the following relationships hold:

$$A = A_{styrene} + A_{pbd} = 10\ (3) + 90\ (4+4x)$$
$$= 390 + 360x$$

$$V = V_{styrene} + V_{pbd} = 0 + 90\ (2-2x)$$
$$= 90\ (2-2x)$$

Since $R = V/A$

$$R = \frac{90(2-2x)}{390 + 360x}$$

The following manipulations are useful:

$90\ (2-2x) = R(390 + 360x)$

note, when $X = 1$; $R = 0$

$X = 0$; $R = 18/39$[a]

---

[a] at $x = 0$; 9 PBD = 18V + 36A

1 styrene = 0V + 3A

18V + 39A

$V = 18$, $A = 39$ So $R = V/A = 18/39$

so the limiting conditions are satisfied.

$$\frac{180}{R} - \frac{180x}{R} = 360 + 30 + 360x$$

$$\frac{180}{R} - 360 - 30 = 360x + \frac{180x}{R}$$

$$180x(2+1/R) = (180\ [1/R - 2]) - 30$$

$$x = \frac{180\ (1/R-2) - 30}{180(1/R + 2)}\ ;\ R = V/A$$

TABLE F3

RATE AND COMPOSITION OF REDUCED SBS-R COPOLYMERS DETERMINED BY IR SPECTROSCOPY

Procedure: The %T at 1601.4 cm^{-1} (styrene only), 965 cm^{-1} (trans butadiene only), 906 cm^{-1} (styrene + vinyl), and at 1650 cm^{-1} (total olefin) were determined from the IR spectra of SBS-R samples. The adsorbance at 1601.4 cm^{-1} was used to correct the adsorbance at 906 cm^{-1} for styrene adsorption. The corrected adsorption at 906 cm^{-1} could then be related to the adsorption at 965 cm^{-1} to give the relative trans vs. vinyl content since the extinction coefficients are known. The overall reduction was found using the 1650 cm^{-1} band.

TABLE F3a

CORRECTION OF 906 cm^{-1} BAND FOR STYRENE ADSORBANCE

Sample	$\%T_{1601.4}$	$A_{1601.4}$	$T_{906.7}$	$(A'corr)_{906.7}$[a]
Polystyrene film .05 mm	20.0	0.70	56	0.25
SBR-2	77.5	0.11	56	0.04
SBR-3	86.0	0.01	56	0.02
SBR-4	92.0	0.04	56	0.01
SBR-5	85.0	0.07	56	0.03
SBR-6	79.5	0.10	56	0.04
SBR-7	82.5	0.08	56	0.03
SBR-8	78.0	0.11	56	0.04
SBR-1				

[a] $(A'corr)_{906.7} = \frac{(A_{1601})\ \text{SBS-R}}{(A_{1601})\ \text{styrene film}} \cdot (A_{906.7})_{\text{styrene}}$

TABLE F3b

ADSORBANCE AT 906.7 cm^{-1} DUE TO VINYL ONLY
NORMALIZED VINYL CONTENT

Sample	$\%T_{906}$	$(A_{906})_{OBS}$	$(A'corr)_{906}$	$(Acorr)_{906}$[a]	Normalized Vinyl Content[b]
SBR-1	65.0	0.19	0.00	0.19	1.02
SBR-2	57.0	0.24	0.04	0.20	1.10
SBR-3	39.5	0.40	0.02	0.38	2.07
SBR-4	60.0	0.22	0.01	0.21	1.14
SBR-5	54.5	0.26	0.03	0.24	1.30
SBR-6	66.0	0.18	0.04	0.15	0.79
SBR-7	83.5	0.08	0.03	0.05	0.27
SBR-8	94.5	0.02	0.04	nil	0.00

[a] $(Acorr) = (A_{906})_{OBS} - (A'corr)_{906}$ is the adsorbance at 906 cm^{-1} due to vinyl only.

[b] Normalized vinyl content $= (Acorr)/(E_{1,2})_{906} \times 10^3$

$1 = (Acorr)/184 \times 10^3$

$(E_{1,2})_{906} = 184$ (80)

TABLE F3c

ADSORBANCE AT 965 cm^{-1}; RELATIVE *TRANS* CONTENT
COMPOSITION OF RESIDUAL UNSATURATION

Sample	$\%T_{965}$	A_{965}	Normalized[a]		Residual Composition[b]	
			Trans Content	Vinyl Content	*Trans*	Vinyl
SBS-R-0	44.0	0.36	2.68	1.02	29.5	70.5
SBS-R-1	44.0	0.36	2.68	1.10	29.5	70.5
SBS-R-2	25.0	0.60	4.52	2.07	31.4	68.6
SBS-R-3	41.5	0.38	2.87	1.14	28.3	71.7
SBS-R-4	35.0	0.46	3.43	1.30	27.6	72.4
SBS-R-5	32.5	0.49	3.67	0.79	17.6	82.4
SBS-R-6	43.5	0.36	2.71	0.27	8.9	91.1
SBS-R-7	70.5	0.15	1.14	0.0	0.0	100.0

[a] Normalized *trans* content $= (A_{965})/(E_{1,4})_{965} \times 10^3$

$= (A_{965})/133 \times 10^3$

$(E_{1,4})_{965} = 133\ (80)$

[b] $\%$ *trans* $= \dfrac{\text{normalized trans content} \times 100\%}{(\text{normalized } \textit{cis} + \text{normalized } \textit{trans}) \text{ content}}$

$\%$ *cis* $= \dfrac{\text{normalized cis content} \times 100\%}{(\text{normalized } \textit{cis} + \text{normalized } \textit{trans}) \text{ content}}$

TABLE F3d

OVERALL REDUCTION OF SBS-R COPOLYMERS DETERMINED BY INFRARED

Sample	$(A_{sty})_{1601}$	$(A_{PBD})_{1650}$	Normalized $(A_{PBD})_{1650}$[a]	% Reduction[b]
SBS-R-0	0.11	0.37	0.36	0
SBS-R-1	0.11	0.35	0.35	5
SBS-R-2	0.07	0.18	0.30	18
SBS-R-3	0.04	0.09	0.28	23
SBS-R-4	0.07	0.13	0.21	43
SBS-R-5	0.10	0.07	0.08	80
SBS-R-6	0.08	0.04	0.06	84
SBS-R-7	0.01	0.01	0.01	98

[a] $$(A_{PBD})_{1650}^{\text{normalized}} = \frac{0.11}{(A_{sty})_{1601}} \times (A_{PBD})_{OBS}$$

Corrects for varying film thicknesses by normalizing with respect to sample SBS-R-0 which defines 0% reaction point; procedure makes series internally consistent.

[b] $$\%\ \text{Reduction} = 100\% \times \left(1 - \frac{A_{PBD}^{\text{normalized}}}{0.365}\right)$$